

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :

C07C 1/20, 1/22

A1

(11) International Publication Number:

WO 96/15082

(43) International Publication Date:

23 May 1996 (23.05.96)

(21) International Application Number: PCT/US95/14397

(22) International Filing Date: 7 November 1995 (07.11.95)

(30) Priority Data:

08/336,430

9 November 1994 (09.11.94)

US

(71) Applicant: STARCHEM, INC. [US/US]; 10822 Fawnview Drive, Houston, TX 77070 (US).

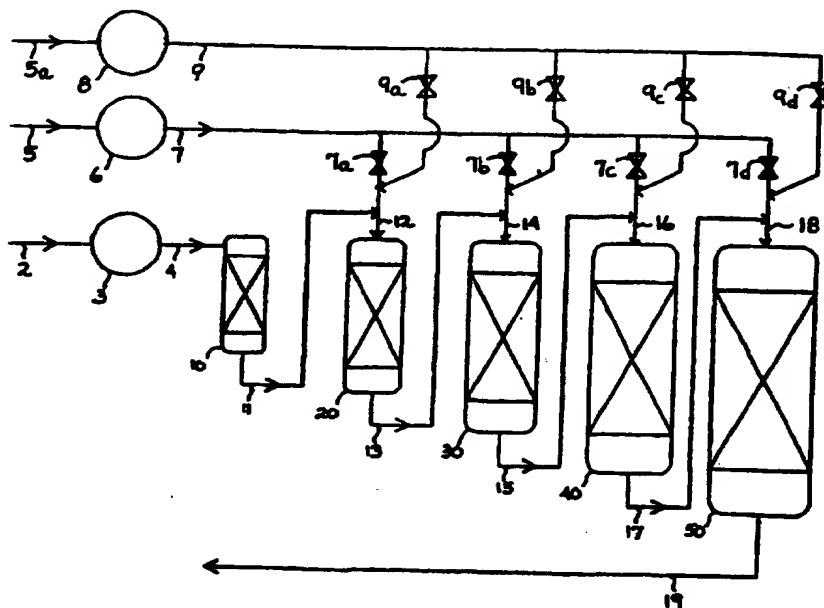
(72) Inventor: VAN DIJK, Christiaan, P.; 10722 Glenway, Houston, TX 77070 (US).

(74) Agents: COX, Charles, M. et al.; Pravel, Hewitt, Kimball &amp; Krieger, P.C., 10th floor, 1177 West Loop South, Houston, TX 77027-9095 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).

**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: CONVERSION OF METHANOL TO GASOLINE



## (57) Abstract

This invention relates to a process for converting alkoxy compounds into hydrocarbon compounds, mostly in the gasoline boiling range. This invention provides energy savings in the conversion of alkoxy compounds compared to conventional catalytic MTG serial fixed bed operations. In this process, fresh alkoxy feedstock (5) is fed to each reaction zone combined with an effluent gas product from a preceding MTG reaction zone (11, 13, 15, 17) together with additional diluent gas (5a). An alkoxy equivalent is provided to each reaction zone in an amount which exceeds that added to a preceding MTG reaction zone from which the effluent product gas was formed. The diluent gas temperature and composition is such that it maintains temperature increases in each successive zone to less than 150 degrees F. and water partial pressures less than 2.2 ata.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LJ	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

-1-

TITLE: CONVERSION OF METHANOL TO GASOLINE

SPECIFICATION

FIELD OF THE INVENTION

This invention relates to a process for converting alkoxy compounds into hydrocarbon compounds, mostly in the gasoline boiling range.

BACKGROUND OF THE INVENTION

Catalysts for the conversion of alkoxy compounds, such as methanol and/or dimethyl ether, to gasoline grade hydrocarbon products have been known since the 1970's.

Processes for the conversion of natural gas and/or coal to methanol have been known for a much longer period.

Since the advent of a catalyst for the conversion of methanol to gasoline as disclosed by various Mobil Oil Corporation patents issued beginning in the 1970's, worldwide only one commercial installation which practices the methanol to gasoline ("MTG") process with a Mobil-type MTG catalyst has come into being. That installation is in New Zealand.

Conceived in the late 1970's when crude oil prices were in the \$30-\$40/barrel range -- with projections for even further price increases -- the New Zealand installation then appeared to be economically feasible. As then envisioned, and as now existing, the New Zealand facility is basically a natural gas to methanol plant (as the front end) coupled to a methanol to gasoline plant operating with an MTG catalyst in a plurality of fixed catalytic bed reactors arranged in parallel, each for single pass gas flow. The arrangement comprises five MTG reaction vessels, four of which operate at any given time and one is off stream for MTG catalyst regeneration or replacement.

Between the conception of the New Zealand facility with its attendant capital and operational cost commitments

-2-

and the time that the facility was completed and ready for on-stream operations (at a capital cost obligation of about \$1.2 billion) the worldwide price of crude oil drastically declined to its current day levels of about \$20/barrel. At today's cost of crude oil, gasoline produced from methanol by a process as followed in the New Zealand facility is competitively uneconomical in comparison to gasoline refined from crude oil. In the first place the New Zealand approach is too costly in the conversion of natural gas into methanol. The present inventor, together with Lowell D. Fraley, has described a natural gas to methanol conversion process with much lower expected capital costs in U.S. Patent Nos. 5,177,114 and 5,245,110. Yet, even with this expected lower cost for methanol the New Zealand process of converting methanol to gasoline is still too high in capital cost. A major reason that the methanol to gasoline part of the New Zealand facility is uneconomical is because of the heat exchange duties -- both in capital and operational cost -- required for proper operation of a Mobil-type methanol to gasoline catalyst (MTG catalyst). For proper operation of an MTG catalyst in terms of its activity and aging, it must be exposed to a particularly controlled environment of temperature and water concentration while it is in contact with the methanol (or other oxygenated compounds) that it converts to gasoline grade hydrocarbons. If exposed to too low of a temperature, an MTG catalyst will not be active or will be of such low catalytic activity to be of no interest. Exposed to too high of a temperature, the MTG catalyst will so prematurely "age" and/or be destroyed so as to be economically impractical for use.

This problem of the temperature sensitivity of an MTG catalyst is compounded by the problem of its need for the presence of water in order for it to be catalytically active. Too little water in its presence and it is inactive or of such low activity to be of little practical interest. Depending upon its temperature exposure, too



-3-

high a concentration of water and the MTG catalyst ages so prematurely and/or is destroyed so as to render its economical use unfeasible.

5 These temperature/water sensitivity problems attendant to use a MTG catalyst are further complicated by the fact that the reaction of methanol (or other oxygenated compounds) to gasoline which it catalyzes is fast and highly exothermic, thus causing a high degree of heat release (i.e., heat of reaction) at the site of the desired  
10 reaction. If not moderated by some means, a methanol and/or dimethyl ether feedstock fed into contact with an MTG catalyst at 710°F would react in contact with the catalyst to form a product gas having a temperature greater than 2,000°F. Such a temperature rise within an MTG  
15 reaction vessel is not acceptable. Nor can the heat released by the MTG reaction be controlled within acceptable product gas exit temperature limits -- i.e., 730°F to 800°F -- by direct heat exchange methods, because the reaction MTG is too fast.

20 The need of an MTG catalyst for a sufficient, though limited, exposure to water coupled with its need for exposure to a sufficient, though limited, range of temperature to be sufficiently active, coupled to the fact that it catalyzes a fast and highly exothermic reaction,  
25 have entailed a number of processing complexities associated to the heat exchange requirements attendant to the proper operation of a methanol to gasoline process with an MTG catalyst.

30 In order to accommodate the temperature range exposure requirements of the MTG catalyst, the New Zealand facility effectuates product gas temperature control within the MTG catalyst vessels by recycle of the C<sub>2</sub>- and C<sub>3</sub>+ hydrocarbon by-product gases remaining after the reactor product gases are cooled down from their reaction temperature of about 800°F  
35 to about 100°F for removal of their gasoline grade hydrocarbon product content. In order to limit the temperature rise in the MTG reaction to less than about

-4-

100°F, this recycle diluent gas is added in an amount compared to the methoxy feed gas (methanol, dimethyl ether, etc.) of about 12.4 moles diluent recycle/mole methoxy equivalent. For every 1 volume of methoxy equivalent with which it is combined to form the feedstock gas it is therefor necessary to heat about 12.4 volumes of the C<sub>2</sub> and/or C<sub>3+</sub> recycled diluent gas from its recovery temperature of about 100°F to the minimum temperature required by an MTG catalyst for sufficient activity, which is about 650°F and preferably about 700°F. This imposes a tremendous heat exchange burden both in terms of reactor effluent gas cool down (800°F to 100°F) for gasoline product recovery and recycle gas (C<sub>2</sub>-/C<sub>3+</sub>) reheat (from 100°F to at least 650°F, and preferably to 700°F). For each volume of hydrocarbon product produced and recovered about 71 volumes of recycle diluent gas must be heated up by about 600°F and later cooled down by about 700°F in adiabatic heat exchanger units by heat exchange first with a new portion of cool feed gas and then by cooling water or a refrigerant.

In the New Zealand operation the methoxy compound, generally in the form of an equilibrium mixture of methanol, dimethyl ether and water vapor, is combined with a recycle gas comprising C<sub>2</sub>-and C<sub>3+</sub> hydrocarbons and the methoxy content is reacted in a single pass over an MTG catalyst to produce a product gas of about 800°F with a partial pressure of water (as steam) of about 2 atmospheres absolute (ata) at a product gas pressure of about 22.3 ata. Hence, heat exchange operations to heat up feed gases and/or cool down product gas are carried out on gas streams at a pressure of about 22.3 ata.

The MTG reaction gases are cooled from their reaction temperature, T<sub>R</sub>, to their final cooldown temperature, T<sub>0</sub>, in two heat exchange operations. In the first operation the reaction gases are indirectly heat exchanged with feed gases through adiabatic heat exchangers to cause the feed gases to warm up from their unit available temperature of

-5-

about  $T_0$  to their reactor inlet temperature  $T_I$  by transferring thereto of a quantity of heat  $Q$  from the reaction gases which thus causes the reaction gases to cool down from their reaction temperature  $T_R$  to their first  
5      cooldown temperature  $T_X$ . Thereafter, the reaction gases are finally cooled from their first cooldown temperature  $T_X$  to the liquid hydrocarbon recovery temperature,  $T_0$ , either by direct or indirect heat exchange contact with chill water.

10      For purposes of discussing the heat exchange burden associated to operation of the New Zealand process, one may assume that the specific heat content of a feed gas about equals the specific heat content of the reaction product gas which results therefrom. Under this circumstance, when  
15      the reaction product gas gives up a quantity of heat  $Q$  to heat up a new portion of feed gas from  $T_0$  to  $T_I$  the reaction gas cools to a temperature  $T_X = T_R - (T_I - T_0)$ . To finally cool the reaction gas to a temperature  $T_0$  to recover its liquid hydrocarbon content the quantity of heat  
20      that must be removed from the reaction product gas is that additional quantity of heat resulting from the heat of reaction of the alkoxy compound from which the reaction gas was formed.

25      Generally, the adiabatic heat exchangers through which feed gas is heated up while reaction product gas is cooled down are on the order of 3-4 times as expensive as those heat exchange units by which the product gas is finally cooled down by heat exchange with chill water. Further, the sizing of each of these heat exchange units, which  
30      bears very significantly on their cost, is directly effected by the difference in temperature to which the feed gases are to be heated and the temperature from which the product gas is to be cooled ( $\Delta T$ ) and the pressure ( $P$ ) of the gases to be heated and cooled. The larger the  
35      differential temperature ( $\Delta T$ ) and/or the higher the pressure the more efficient the heat exchange process and the smaller can be the size of the heat exchanger needed.

-6-

The relative heat exchange surface area ( $A_R$ ) required to transfer this quantity of heat ( $Q$ ) is generally given by the formula  $A_R = Q (1/\Delta T)(1/P)^{0.6}$ .

5 Suggestions have appeared in the prior art which are directed to ameliorating this tremendous heat exchange burden. Mobil Oil Corporation's U.S. Patent 4,035,430 to Dwyer et al. describes an MTG process wherein a number of spaced apart MTG catalyst beds are employed and hydrocarbon recycle gas may be injected between the successive beds to control the exotherm. Also described is the possibility of interbed injection of methanol or DME as a quench to maintain the temperature rise in each MTG catalyst bed to about 50°F with a total temperature rise over all beds to about 200°F. This however, as Mobil's later U.S. Patent 15 4,404,414 to Penick et al. notes, requires either that the conversion of the alkoxy feed in each MTG reactor be limited to a relatively low value (which is difficult to control at the high reaction rate in contact with the catalyst) or, alternatively, that an extraordinarily high recycle ratio must be used, neither being an attractive possibility.

Mobil's U.S. Patent No. 4,404,414 to Penick et al. provides yet another suggestion. It describes the use of the reactor effluent gas of a preceding MTG reactor, for admixture with a fresh charge of alkoxy compound (DME and/or methanol) to be fed to a succeeding MTG reactor, as the medium for heating up the new alkoxy charge of combined gas mixture to the inlet temperature desired for reaction in a succeeding MTG reactor. According to Penick et al.'s suggestion the total quantity of temperature-control diluent gases used in the process is passed through the first MTG reactor and hence into the succeeding MTG reactor without the need for cooldown heat exchange of the diluent gas from the reaction gas temperature (about 800°F) to about 100°F for purposes of product recovery and thereafter reheat from about 100°F to an inlet reaction temperature (about 700°F) for recycle use with the new alkoxy charge.

-7-

This reduces the overall effective volume of recycle gas as a ratio to the final product make required for proper temperature moderation in the MTG reactors. However, this heat exchange savings is purchased at the risk of advanced aging of the MTG catalyst in the succeeding MTG reactor that may result from the successive accumulation of water (steam) content that results from the buildup of water as a by-product of the MTG reaction that occurs within both the preceding and succeeding reactors. For example, for each mole of hydrocarbon produced, the hydrocarbon product from crude methanol having a water content of about 6 wt.% or from an equilibrium methanol-dimethyl ether mixture produced therefrom contains about 6.45 moles of water. Addition of a diluent gas to this methoxy compound in an amount sufficient to moderate the temperature rise in a first MTG reactor as desired, followed by addition to the first reactor product gas of an equivalent amount of new methoxy compound to form a feed gas stream for reaction in a second MTG reactor results in a product gas from the second reactor having nearly double a mole fraction of water as that of the product gas from the first MTG reactor.

Accordingly, in the process proposed by Penick et al. where both reactors are operated at about the same pressure the concentration of water (as steam) to which the MTG catalyst of the succeeding MTG reactors is subjected is substantially greater than that to which the MTG catalyst of the preceding MTG reactor is exposed. This, as Penick et al. notes, inevitably leads to the dilemma that if both reactors are operated at about the same temperature either the MTG catalyst in a preceding MTG reactor must be under-utilized by depriving it of exposure to a water content that optimizes its potential for activity or the MTG catalyst in a succeeding MTG reactor must be overexposed to water such that it ages prematurely. This dilemma of Penick et al.'s proposal necessitates a significant difference in the operational conditions of temperature or

-8-

pressure between the preceding and succeeding MTG reactors, which, in order to maximize both the activity and operational life of the MTG catalyst in each, results in an undesirable change in hydrocarbon product's compositional distribution produced in each.

Yet another Mobil Oil Corporation U.S. Patent No. 4,788,369 to Marsh et al. suggests a method for improving the economies of even the Penick et al. process that involves the separation of the  $C_{3+}$  by-product hydrocarbon gases from the  $C_2$ -by-product hydrocarbon gases and thereafter use of the  $C_{3+}$  hydrocarbon gases as the recycle diluent gas required for temperature moderation. Because of the higher specific heat of the  $C_{3+}$  recycle, following the suggestion of Marsh et al. the volume of recycle diluent gas required for practice of the MTG process may be reduced. As Marsh et al. notes, in terms of compressor duties a  $C_{3+}$  recycle gas is more readily and economically processable for recycle use than is a  $C_2$ - recycle gas. However, a smaller amount of the  $C_{3+}$  recycle gas volume necessitates use of a lower total pressure for processing if the steam vapor pressure is to be kept the same as before. That lower pressure has a negative effect on the heat exchange capability of the process. Thus, the only advantage remaining for the Marsh approach is the use of fewer moles of recycle gas which thus reduces compressor duties. The disadvantages of increased heat exchange surface requirements resulting from the lower pressure of operation reduces, and might even outweigh, the savings in the recycle compressor. It suffices to say that the Marsh et al. patent does not succeed in diminishing the heat exchange requirements of the process. Yet, even with use of a  $C_{3+}$  hydrocarbon by-product gas as a recycle to save on compressor duties as suggested by Marsh et al. the savings in capital and operational cost of the Marsh et al. process requirements are modest, at best.

The temperature rise/water concentration dilemma that hampers the MTG conversion process over an MTG catalyst

-9-

as being an economically competitive process for gasoline production compared to that of gasoline refined from natural crude oil remains unsolved by any prior art suggestion. Given the abundance of natural gas reserves from which the production of gasoline grade products is technologically possible, a solution to the economical obstacle to its conversion to gasoline is a greatly desired goal.

#### SUMMARY OF THE INVENTION

In accordance with the process described by this invention, it is possible to substantially reduce the heat exchange duties entailed in the proper operation for activity and aging regulation of an MTG catalyst while also properly controlling the exposure of such catalyst to a water concentration.

To significantly reduce the heat exchange requirements for proper temperature control of the reaction of an alkoxy compound over an MTG catalyst, and at the same time control the steam partial pressure in the process within narrow limits, aiming thus to have the reaction proceed under proper temperature and steam pressure control without at any time endangering the MTG catalyst, the invention proposes a method for operation of an MTG process wherein:

(1) Successive reaction zones containing an MTG catalyst are employed wherein a product effluent gas of temperature  $T_{r_p}$  from a preceding MTG reaction ( $r_p$ ) is combined with a new charge of feed gas comprising an alkoxy compound and a diluent gas comprising a  $C_2$ -recycle gas, a  $C_3+$  recycle gas, steam, hydrogen, or mixtures thereof, which new charge of feed gas has been preheated to a temperature  $T_p$  that is less than  $T_{r_p}$ , and the mixture of the new charge of feed gas with the product effluent gas forms a combined gas mixture that is of a desired temperature  $T_i$  and specific heat content to be contacted with an MTG catalyst in a succeeding reaction zone ( $r_s$ ) to convert its alkoxy compound content to hydrocarbon products contained in a new product gas stream having a temperature

-10-

Tr<sub>s</sub>. In warming up the new alkoxy-recycle feed gas charge from the preheat temperature T<sub>p</sub> by mixing with the earlier hot effluent gas to obtain a combined gas mixture of temperature T<sub>i</sub> the warmup is obtained without heat exchangers, which otherwise would have been necessary to warm the new feed gas up to the desired reactor inlet temperature; further the lower diluent recycle content of the fresh feed gas would not allow entry of that feed as such at the desired reactor inlet temperature without its reaction to a temperature greater than the Tr<sub>s</sub> temperature desired for the outlet from the reactor.

(2) The new charge of alkoxy compound provides an alkoxy equivalent value which exceeds that which was added to the preceding MTG reaction zone and the new charge of diluent gas provides the combined gas stream with a specific heat content that upon reaction of the new charge of alkoxy compound to hydrocarbon compounds limits the temperature rise ( $\Delta T_R$ ) within the succeeding reaction zone to less than 100°F and preferably less than 75°F.

(3) The new charge of alkoxy compound and diluent gas are preheated before combination with the product effluent gas to a temperature T<sub>p</sub> that is below the desired reactor inlet temperature T<sub>i</sub>, so that on taking an appropriate amount of this new charge for addition to the effluent gas from the preceding reactor a mix temperature of T<sub>i</sub> will be obtained, whereafter contacting the combined gas mixture with a sufficient amount of MTG catalyst the succeeding reaction will produce a new effluent gas temperature of T<sub>R</sub>, which is at a desired level. As desired, each MTG reactor in the series may be operated with the same T<sub>i</sub> and T<sub>R</sub> temperatures or any reactor within the series may be operated at a T<sub>i</sub> and T<sub>R</sub> temperature selected for it which is different than that of other reactors in the series, this being accomplished by the proper choice of the alkoxy and recycle content of the new feed gas charge to be added to the succeeding reactor and the quantity of this new feed



-11-

charge to be combined with the product effluent gas from the preceding reaction.

(4) As desired, a portion of the new charge of diluent gas may comprise water in an amount that together with the water carried over with the product effluent gas and the water formed by reaction of the new charge of alkoxy compound provides a total water content in the new product effluent gas that at the outlet pressure of the succeeding MTG reaction zone provides for any partial pressure of water desired, which preferably will not exceed 2.2 ata, and preferably will be in the zone of 1.85 to 2.2 ata, most preferably in the zone between 1.95 and 2.15 ata.

In its general form the process of this invention may seem complicated with respect to how the process conditions can be set and kept at necessary conditions in order to achieve the desired goal. Therefore the invention will first be explained in its simplest form. Assume that it is desired to have a series of reactors, in all of which the reaction of the methoxy compounds is taking place in the same reaction temperature zone ( $T_1$  to  $T_R$ ) and also where all the reaction product gases have identical steam vapor pressures.

This target can be achieved even though substantial pressure drops exist between reactor zones. Again, it is easier to explain the invention if the simplifying assumption is made that the pressure drop between reactors is so small that it can be ignored.

It is clear that given a chosen composition of the diluent recycle, conversion of a given amount of a given methoxy compound can be kept in a single reactor in a desired reaction temperature zone, say from 700 to 800°F, by proper choice of the quantity of the diluent recycle gas added to the methoxy compound. Choose now, however, a smaller quantity recycle gas, which would then necessitate a larger reaction temperature zone, but with the same final temperature, say between 600 and 800°F. Also choose a pressure at which to operate so that on reaction the

-12-

resulting water vapor partial pressure is at the desired level.

Now take a large quantity of such an alkoxy-recycle gas mixture and preheat that to the temperature of 600°F, but do not as yet contact the so preheated gas with the MTG catalyst. Take a starter gas stream at the desired final temperature level of 800°F with the desired level of water vapor partial pressure at the desired total pressure. Such a starter gas stream could be of any composition, but could conveniently be made from the same alkoxy compound in admixture with a similar diluent recycle composition, but in a larger recycle amount, so that that the starter stream could be warmed up to 700°F and contacted with MTG catalyst to react to a product gas having a temperature of 800°F.

Now take of the new mixture of alkoxy and recycle that has been preheated to 600°F, and in a sufficient amount mix it with the hot starter gas stream which is at 800°F to arrive at a combined gas stream having a temperature of 700°F. On reaction of the alkoxy content of the combined gas stream over an MTG catalyst the final temperature of the product gas will then be 800°F, because each component part of the combined gas stream was once at or could react to this temperature.

The product gas stream at 800°F, thus obtained, serves in its own turn as a hot gas source for admixture with a new portion of the 600°F gas mixture containing new alkoxy compound to arrive at a still larger volume 700°F combined gas stream which again can be contacted with an MTG catalyst to form a product gas stream at 800°F. This alternating mixing and reaction is continued until all the alkoxy containing gas mixture of 600°F has been reacted.

When pressure drop across the MTG reactor(s) is sufficiently large to have to be taken into account; then on each addition of the 600°F alkoxy-containing gas a sufficient amount of steam may be added also, so as to arrive at the desired water partial pressure at the resulting lower total pressure due to pressure drop. A

-13-

reduction is then needed of the amount of the diluent recycle gas content of the new charge by an amount that corresponds to the specific heat content of the added steam, so that the (slightly) changed 600°F stream still  
5 will be able to react to 800°F. Alternatively, with no alteration of the alkoxy-containing gas mixture, the same results can be obtained by adding the requisite amount of 800°F steam to the product effluent gas or to the 600°F alkoxy-containing gas.

10 The given procedure can obviously also be applied to a narrower reaction temperature zone than 700 to 800°F and to different starting temperatures for the gas mixture subjected to reaction than the value of 600°F chosen for this discussion.

15 It is also clear that it is possible to vary the steam partial pressure from reactor to reactor, if desired. Such steam partial pressure variations are easier in an upward direction than downward.

20 A further advantage is that the temperature zone of reaction can be varied at will from reactor to reactor by changing the amount added of the new alkoxy-recycle charge and its preheat temperature.

25 It should therefore be clear, that this invention provides a feasible method to have the MTG reaction proceed within desired limits of temperature and also attain the desired water vapor partial pressure levels in the exit of each of the reactors.

30 It is the primary intent of this invention to lower the cost of the heat exchange which is a major cost item in the New Zealand design. However, it should also be pointed out that the present invention opens the possibility for operating a series of reactors under an innovative temperature and steam partial pressure approach.

35 It has been discussed in the literature that at low temperature a large percentage of aromatic hydrocarbons are formed in the MTG reaction. When the MTG reaction then proceeds to higher temperatures, the aromatics previously

-14-

formed are alkylated with the methanol which is still being reacted at these higher temperatures. When it is desired to lower the content of higher alkylated aromatics, like durene and even the trimethylated benzenes (as presently  
5 desired for achieving a high quality reformulated gasoline), with this invention it then becomes feasible to operate the first set of MTG reactors at a higher inlet temperature, thus lowering the formation of aromatics to a very low amount and only in the last MTG reactor allowing  
10 operation at a lower temperature, but finishing the reaction in that lower temperature zone. This thus translates to an operation of the first four of, say five, reactors at a temperature zone of for instance 720 to 790°F, while the last MTG reactor can be kept within the  
15 narrow temperature limits of for instance 700 to 740°F. The larger amount of aromatics formed in the last reactor can then not be further alkylated above the 740°F temperature.

According to this invention the total amount of alkoxy  
20 equivalent processed to hydrocarbon products is proportioned among a plurality of MTG reaction zones and the alkoxy equivalent quantity provided to each MTG reaction zone generally increases in progression from the first to the last or final MTG reaction zone. This method  
25 of operation provides for great flexibility in the operational conditions of temperature and pressure at which a given MTG reaction zone may be operated relative to another in order to achieve a variety of desirable objectives, all attendant with a significant reduction in  
30 the heat exchange duties otherwise required to process the same total amount of methoxy equivalent to hydrocarbon products by prior MTG processing methods.

For instance, where the activity of the MTG catalyst is the same in each zone, for uniformity of product  
35 distribution of hydrocarbon product produced in each MTG reaction zone, each desirably is operated at approximately the same pressure, the same inlet and outlet temperatures

-15-

(i.e., each zone has the same  $\Delta T_R$ ), and each reaction zone, at least after the first, has about the same partial pressure  $H_2O$  at the outlet of the reaction zone. Such is possible with the method of the invention. However, if  
5 because of aging or other reasons the activity of an MTG catalyst in one of the multiple zones is significantly less than another, it may be desired to operate this particular MTG reaction zone at a higher outlet partial pressure of  $H_2O$  than the other, or at a higher  $T_R$ , this in order to  
10 enhance the activity of the MTG catalyst therein. This too is possible with this invention.

A combination of factors leads to a significant reduction in the heat exchange duties required by the process of this invention in comparison to prior MTG  
15 processes employed or proposed. First, on the bases of the total methoxy equivalent ("MeO eq.") processed, with the process of this invention the diluent gas/MeO eq. mole ratio is reduced which in turn reduces the quantity of diluent gas that through adiabatic heat exchange units must  
20 be preheated for reaction temperature moderation use or, ultimately, cooled down for recovery of hydrocarbon product. This reduces the size of the heat exchangers required for feedstream heatup and/or final product cooldown. Further, a significant quantity of the total  
25 methoxy equivalent processed, together with the recycle diluent gas needed to moderate its heat of reaction, needs to be preheated to a temperature ( $T_P$ ) which is lower than the temperature ( $T_I$ ) at which it is desired to contact the methoxy compound with an MTG catalyst. This is achieved by  
30 admixing the methoxy-recycle feed with hot product gases from a preceding MTG reaction (at  $T_R$ ) which heats up the added methoxy-recycle feed to the desired reaction inlet temperature, while cooling down the hot reaction gases to the desired reaction inlet temperatures. In this respect  
35 this aspect of the feed gas heatup/product gas cool down is performed by direct gas-gas contact, thus eliminating this portion of need for adiabatic heat exchange equipment.

-16-

Also, with respect to the warmup of feedstock gases to  $T_p$  by heat exchange with reaction gases at  $T_R$  through an adiabatic heat exchanger, this also increases the heat exchanger differential temperature ( $\Delta T$ ) making the heat exchange process more efficient, meaning the heat exchanger need will be smaller.

As explained hereafter in greater detail, operations in accordance with this invention permit a selection of conditions in terms of (a) the nature of the methoxy feed, (b) the nature of the diluent gas composition, and (c) the temperature to which the feed gases are preheated before being mixed with reaction gases from a preceding MTG reaction; such that the MTG conversion can be achieved with the maximum of economy in terms of the capital and/or operational cost associated therewith.

#### DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a five reactor series with interstage feed of feed charges of alkoxy-recycle feedstock gases between the reactors in accordance with the present invention.

Figures 2 and 3 plot the effect on the required relative heat exchanger surface area ( $A_r$ ) required for performing feed gas warmup by product gas cooldown heat exchange operations in adiabatic heat exchange units in accordance with the process of the invention for different preheat temperatures  $T_p$  as employed in a series of from five to ten MTG reactors, wherein a pressure drop of 0.35 ata occurs across each reactor. The relationships illustrated are based upon the general equation  $A_r = Q(1/\Delta T)(1/P)^{0.6}$  wherein  $Q$  is the quantity of heat involved in a heat exchange operation;  $\Delta T$  is the temperature difference between the gases involved in the exchange, namely  $T_R - T_p = \Delta T$ ; and  $P$  is the pressure of the gases being heat exchanged. The alkoxy feed for Figure 2A is dimethyl ether (DME) and for Fig. 3 is a DME containing equilibrium mixture formed from a crude methanol containing 16.4 wt.% water. For comparison treatment of the same

-17-

quantity of an equilibrium mixture formed from methanol-water in a single reactor requires a relative heat exchange surface area of about 325.4 relative units when operated at a pressure of 22.06 ata to provide for the same partial pressure of steam in the product gas as that provided by the process as illustrated in Figure 3.

Figure 4 is a schematic illustration of an alternative embodiment of the process wherein the first of a series of five MTG reactors recycles a portion of its product gas back to the inlet of this first MTG reactor to provide a gas-to-gas exchange of heat with fresh alkoxy feed to this reactor to achieve its final warmup from its  $T_p$  temperature to the  $T_i$  temperature desired for contact with the MTG catalyst therein.

#### 15 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The practice of this invention requires an alkoxy feedstock, generally a MeOH and/or DME feedstock, various reaction vessels containing an MTG catalyst composition and devices for controlling the rate of feed of DME and/or MeOH and  $H_2O$  (as steam),  $C_2$ - and  $C_3$ + gas by-product as diluent recycle gaseous feedstock admixture components of the total feedstocks to an MTG catalyst containing reaction vessel.

The MeOH may be formed from a coal or natural gas starting material by any of the methods well known to those skilled in art. Preferably when produced from natural gas the methanol is produced by methods as described in U.S. Patent Nos. 5,117,144 and 5,245,110. Prior to the MTG reaction, and preferably so, the MeOH may be subject to contact with a dehydration catalyst as is well known in the art to convert it to an equilibrium mixture of MeOH, DME and  $H_2O$  and this gaseous mixture of oxygenated organic components which is a preferred alkoxy feed component for an MTG catalyst contact for conversion to a hydrocarbon product with production of by-product water. Most preferred is the use of DME alone as the alkoxy feed component. DME can easily be isolated from the equilibrium mixture and the remaining methanol-water can be

-18-

concentrated as to its methanol content and recycled back to contact with the dehydration catalyst to make more DME containing equilibrium mixture.

5 The MeOH and/or DME components, however made, are, in the process of this invention, brought into contact with an MTG catalyst composition, as described in U.S. Patent Nos. 4,404,414; 4,788,369 to Penick and Marsh as earlier discussed and in other Mobil U.S. patents, to catalyze their conversion into a hydrocarbon product, a significant  
10 portion of which is within the gasoline boiling point range. As a rule of thumb, the carbon atoms supplied by the methoxy content of the DME/MeOH feed gas composition are converted to a hydrocarbon product averaging a carbon atom content of about 5.8 -- i.e.,  $C_{5.8}H_{13.6}$ . This  
15 hydrocarbon product is, of course, comprised of a mixture of hydrocarbons which vary in carbon atom numbers from one up. The  $C_{1-3}$  carbon atoms products of this reaction are normally gaseous compounds and are recovered and at least a portion thereof is recycled as a diluent gas to become a  
20 part of a fresh alkoxy feedstock to an MTG reactor, together with traces of higher hydrocarbons. Most of the  $C_{5+}$  carbon atom hydrocarbon products are recovered as a "gasoline" or fuel grade product. The  $C_{2-}/C_{3+}$  hydrocarbon gas by-products of the MTG reaction which are recovered may  
25 be separated into separate  $C_2$ -and  $C_{3+}$  streams, and either alone or in desired combinations thereof recycled to the MTG process for purposes of temperature control.

In order to minimize the heat exchange duty requirements while regulating the temperature, pressure and  
30 water concentration conditions for the proper activity and aging regulation of an MTG catalyst during the conversion of alkoxy compounds to hydrocarbon products, the process of this invention utilizes a plurality of MTG catalyst zones or reaction vessels in series flow whereby the product  
35 effluent gas from any preceding MTG zone or reactor is combined with a fresh charge of alkoxy compound together with a recycle diluent gas and/or water (stream) to form a



-19-

combined gas steam of a temperature and specific heat content suitable as an alkoxy-containing feed gas to a succeeding MTG zone or reactor wherein its alkoxy compound content is reacted in contact with an MTG catalyst to hydrocarbon compounds. Generally, the alkoxy equivalent of the alkoxy compound added to the product effluent gas of a preceding MTG reaction exceeds the alkoxy equivalent content of the feed gas stream to the preceding reactor from which the product effluent gas was produced.

Any number of MTG reaction zones or reactors may be utilized, though generally no further practical advantage is realized in excess of ten, and more preferably five to eight MTG reaction zones or reactors in series. The product effluent gas from the final MTG reaction of the series is cooled from its final reaction temperature to about 100°F to recover its liquid hydrocarbon content separate from its C<sub>2</sub>- and C<sub>3+</sub> gaseous hydrocarbon content. At least a portion of C<sub>2</sub>- and/or C<sub>3+</sub> gaseous hydrocarbon by-product is recycled for use as a temperature moderating diluent gas for combination with fresh charges of alkoxy compound and the recovered liquid hydrocarbon is further refined into its various boiling point fractions for use as fuels or other purposes.

The combination of a fresh charge of alkoxy compound and C<sub>2</sub>- and/or C<sub>3+</sub> recycle gas with the product effluent gas from a preceding MTG reaction to form a combined gas of suitable inlet temperature (T<sub>1</sub>) and specific heat content as feed to a succeeding MTG reaction reduces the overall heat exchange duties with respect to the total make of hydrocarbon product by reducing the size of the heat exchangers needed for heating the fresh charge to the temperature to which the fresh charge of alkoxy compound and recycle gas must be preheated to condition it for admission to the succeeding MTG reactor, which mixture in line with its alkoxy content and its total specific heat content will react in contact with an MTG catalyst from a

-20-

temperature of  $T_i$  to the desired temperature  $T_R$  for the new reactor.

For example, conversion of 100 MPH of methanol (MeOH) creates a heat of reaction ( $Q_R$ ) of  $100 \times 24,000$  BTU/lb-mole MeOH = 2,400,000 BTU. To limit the temperature rise of the reaction gases to  $\Delta T_R = 75^\circ\text{F}$  for a gas inlet temperature  $T_i = 710^\circ\text{F}$  and an effluent gas outlet temperature  $T_R = 785^\circ\text{F}$  the total specific heat content of the feed gas must be  $2,400,000/75 = 32,000$  BTU/ $^\circ\text{F}$ . Hence recycle diluent gas is combined with this methanol in an amount to provide a total feed gas of this specific heat content. To preheat this total feed gas from its unit available temperature  $T_0$  of, say,  $100^\circ\text{F}$  to the reactor inlet temperature  $T_i$  of  $710^\circ\text{F}$  requires the addition of heat to such gas that is

$$(710-100) \times (32,000) = 19,500,000 \text{ BTU.}$$

On the other hand were a quantity of recycle diluent gas added to this methanol that would allow it to increase in temperature by  $150^\circ\text{F}$  due to the reaction of methanol, the total feed gas would have a total specific heat content of  $2,400,000/150 = 16,000$  BTU/ $^\circ\text{F}$ , meaning there would be less recycle diluent gas added. This feed gas could then react from a temperature of  $635^\circ\text{F}$  to a product gas of  $785^\circ\text{F}$ . Then to preheat this total feed gas stream from  $100^\circ\text{F}$  to  $635^\circ\text{F}$  would require the addition of heat of  $(635-100) \times (16,000) = 8,560,000$  BTU. By mixing this  $635^\circ\text{F}$  temperature gas having a specific heat content of  $16,000$  BTU/ $^\circ\text{F}$  with a gas stream having a temperature of  $785^\circ\text{F}$  and a specific heat content of  $16,000$  BTU/ $^\circ\text{F}$  a combined gas stream is formed having a temperature of  $710^\circ\text{F}$  and a total specific heat content of  $32,000$  BTU/ $^\circ\text{F}$ . Thereafter, reaction of the methanol content of this combined gas stream will increase the temperature of the gas by  $2,400,000/32,000 = 75^\circ\text{F}$  to provide an effluent gas stream having an outlet temperature  $T_R$  of  $785^\circ\text{F}$ .

As seen from the above, the quantity of heat exchange required for warmup of the feed gas is significantly reduced because the quantity of recycle diluent gas is

-21-

reduced, but the methanol is still converted in the same temperature zone, i.e., 710-785°F. Further, the efficiency with which the feed gas warm-up heat exchange is accomplished is significantly enhanced by reason of the increase in the differential temperature ( $\Delta T$ ) at which the heat exchangers performing this duty operate. On one hand, the 710°F warm-up situation would require a heat exchanger surface area ( $A_R$ ) of  $A_{R710} = 19,500,000 (1/P_{710})^{0.6}$  and the 635°F warm-up situation would require  $A_{R635} = 8,560,000 (1/P_{635})^{0.6}$ . The savings in heat exchange duties to be realized through the change in the differential temperature of heat exchange operations would only be offset if the difference in the pressure (P) of the two operations were such that for the 635°F warm-up situation the pressure for operation was less than one-twelfth (1/12) that for operation of the 710°F warm-up situation.

However, the change in the recycle GAS amounts between the two situations does not require such drastic reduction in the pressure of operation in order to maintain the same partial pressure of steam in the two product gases.

In these embodiments of the process of this invention wherein the first MTG reactor of the series operates on a feed gas composition that is preheated through adiabatic heat exchangers to the  $T_i$  temperature desired for its contact with the MTG catalyst therein, the heat exchange duty that this reactor contributes to the total heat exchange duty of the overall process is significantly greater in comparison to the quantity of methoxy equivalent converted therein than is that contributed to the total by the subsequent MTG reactors of the series. Hence, by using a larger number of reactor steps, the influence on the total heat exchange duties of the warmup for the first reactor is greatly reduced so that the benefit for the reduction in heat exchange for the subsequently added feed gas material is then almost totally available as the gain for this reaction choice. The number of reactors utilized together with the conditions chosen for their operation is

-22-

preferably such that no more than 20% of all alkoxy compound converted by the process is converted in the first reactor of the series, preferably no more than 10%. As made clear in the examples, the reduction of the total heat exchange duties in comparison to that for a single reaction stage processing of the same quantity of methoxy equivalent is substantial and can be as much as a reduction by about an order of magnitude of.

The heat exchange is further facilitated by using an alkoxy feed which will make a lower steam fraction and can therefore be used at higher pressure, which facilitates the heat exchange. Such feeds may be obtained by removing water from the alkoxy feed. Removing water from methanol is possible by distillation but that is a rather difficult operation. It is easier to remove steam from dimethyl ether, which can easily be made from methanol by contact at high temperature over an acid catalyst like alumina. The then unconverted methanol and most of the water present can easily be separated from the DME and recycled back to the DME conversion reactor. Use of the DME as the alkoxy feed for hydrocarbon production reduces the amount of water generated in the MTG reaction to only 0.5 mole water per mole of alkoxy equivalent, as against 1.3 for a methanol stream containing 30% of this methanol molar content as water.

Another means for increasing the efficiency of the heat exchange operations required is to employ a diluent gas composition containing low molecular weight species, like hydrogen, and/or species of a low specific heat value. Hydrogen for addition to the  $C_2$ - and/or  $C_3$ - diluent recycle gas can be provided out the methanol production unit by diffusion of the tail gas therefrom through a membrane preferential for permeation of  $H_2$  relative to other gas species. Further, use as a diluent gas of a recycle which is rich in the  $C_2$ - hydrocarbon by-product allows operations at a higher total pressure while providing for the same partial pressure of steam in the product gas than does a

-23-

diluent gas rich in the  $C_3+$  hydrocarbon by-production. The higher operational pressure provided by use of a  $C_2$ -rich recycle provides for more efficient heat exchange of the feed and product gases by a factor of  $(1/P)^{0.6}$ .

5 With the process of this invention the operation of each MTG reactor in the series at the same inlet and outlet temperatures and at about the same partial pressure of steam at the outlet without significant changes of pressure therebetween becomes possible (i.e., allowing only for the  
10 pressure drop across each reactor needed for gas flow) -- thus providing for uniformity of product distribution production in each of the reactors. For example, with reference to use of dry methanol as the fresh alkoxy feed for each MTG stage, wherein the quantity of methanol feed  
15 doubles with each succeeding stage, when dry methanol is used as the first stage feed the partial pressure of water in the product gases of the early MTG stages is significantly lower than that of the later MTG stages. Hence, wherein the last MTG stage is operated at an outlet  
20 pressure that provides for a partial pressure of water of 2 ata, the first MTG stage operates at an outlet pressure that provides a partial pressure of water of about 1.015 ata. However, by adding water (steam) to the dry methanol feed to the first stage, and/or as needed or desired in the  
25 fresh methanol feed to later MTG stages, it is possible to operate each MTG reactor at substantially the same partial pressure of water at its outlet without significantly reducing the pressure at which the last MTG reactor operates. It is also possible, as desired, to operate a  
30 succeeding reactor at a condition of an inlet-outlet temperature or a pressure that significantly differs from the operating conditions of preceding reactors without exceeding a partial pressure of steam therein that would prematurely age or destroy its MTG catalyst content -- to  
35 permit the control of final product distribution, such as to minimize the durene content of the hydrocarbon product.

Nature of the Alkoxy Feed

-24-

Whatever the precise nature of the alkoxy feed, typically it will be available for use at about 100°F following its production and cooling to condense excess water from it. Although an MTG catalyst is active for production of hydrocarbon products with respect to any alkoxy compound -- i.e., alkanols, alkylethers, and combinations thereof -- and the process of this invention is applicable to the use of any suitable alkoxy compound; conventionally the alkoxy compound used is methanol, dimethylether, or equilibrium mixtures thereof produced by the catalytic dehydration of methanol. Hereafter, the process of this invention is described with respect to methoxy compounds -- i.e., methanol (MeOH), dimethylether (DME), and mixtures thereof (MeOH + DME). Further, reference to the amount of hydrocarbon products of which the methoxy compound is capable of production is referred to by its "methoxy equivalent." For example, for a hydrocarbon product having an average carbon number value of 5.8 carbon atoms, the following equations apply:



Hence, each mole of MeOH presents one methoxy equivalent and each mole of DME presents two methoxy equivalents.

Within the context of this invention the methoxy compound employed as feed may be methanol only, dimethyl ether only, or mixtures thereof together with such water vapor content as is normal to their production or, preferably, after water that is condensable at about 100°F has been separated therefrom. The nature of the methoxy composition selected as fresh feed to an MTG reactor affects the nature and/or quantity of diluent gas with which it must be combined for proper moderation of the temperature rise and water concentration control within an MTG reactor. On a methoxy equivalent basis, each mole of MeOH releases a greater quantity of heat (24,000 BTU/lb-mole) and H<sub>2</sub>O by-product (1 mole H<sub>2</sub>O/mole) than does DME (1/2 mole H<sub>2</sub>O/mole and 35,200 BTU/lb-mole). Further, since

-25-

the specific heat of MeOH (16.94 BTU/°F/lb-mole) and DME (25.08 BTU/°F/lb-mole) differ, the composition of the methoxy feed selected influences the degree to which the methoxy + recycle diluent gas composition must be preheated before its admixture with the product effluent gas from a preceding MTG reactor to yield a combined gas stream of suitable temperature and specific heat content for feeding to a succeeding MTG reactor.

An ideal case for purposes of achieving the greatest economics in the overall heat exchange requirements for the hydrocarbon production process is that of exclusive use of DME as the methoxy compound. Next in order of preference is that of the use of a dehydration equilibrium mixture of MeOH + DME as the methoxy feed.

#### The MTG Catalyst

A variety of compositions have been disclosed as suitable catalysts for the conversion of methoxy compounds to hydrocarbon compounds, as for instance in U.S. Patent Nos. 3,702,886; 3,709,979; 3,832,449; 3,998,889, 4,076,842; 4,016,245 and 4,046,859, the disclosures of which are herein incorporated by reference. Further, this invention is applicable to any composition now existing or which may be developed which catalyzes the conversion of alkoxy compounds to hydrocarbon products, especially wherein the catalyst composition exhibits a similar sensitivity to temperature and water concentration in terms of its activity and aging characteristics as now existing MTG catalyst compositions do.

Whatever MTG catalyst composition is selected for use, for essentially complete conversion of the methoxy compound to hydrocarbon to occur, the methoxy containing feed gas must first be conditioned to have about at least a minimum inlet temperature ( $T_i$ ) of about 650°F, and preferably about 700°F. Further, the feed gas should have a specific heat content that limits the temperature increase ( $\Delta T_R$ ) between the inlet temperature ( $T_i$ ) and outlet temperature ( $T_R$ ) of the MTG reactor to less than 100°F, preferably 85°F or less.

-26-

The inlet gas temperature may range from about 650 to 720°F to insure complete conversion, while the outlet temperature should be limited to a range of from about 730-800°F. To prevent premature aging or damage of the MTG catalyst a temperature of 800°F should not be exceeded. Also, the partial pressure of steam at the outlet should be limited to a range of 1.85 to 2.2 ata, and preferably 1.95 to 2.15 ata.

Within the broad ranges of inlet and outlet temperature, various narrower ranges are preferred for purposes of product composition and distribution. For example, the amount of durene -- an undesirable hydrocarbon component for purposes of fuel uses -- has been found to vary with the reaction temperature, increasing with lower reaction temperatures and decreasing with higher temperatures. Accordingly, to minimize durene content while maximizing the fraction of liquid hydrocarbon and the octane value of the liquid hydrocarbon fraction an inlet temperature of at least about 700°F is preferred. To further insure against premature catalyst aging or destruction a temperature of 785°F and partial pressure of steam of 2.2 ata at the reactor outlet is preferably not exceeded.

The improved process is based on adiabatic reaction in a multiple reactor system with intermediate injection of colder feed. While the different reactors can easily operate under different conditions, it is easier to explain the new process and its advantages by discussing the special case of all reactor steps operating under similar conditions as to the temperature zone for the contact with the catalyst and the final steam vapor pressure of the reactants in each reactor.

As a typical set of conditions by which to illustrate practice of the process of this invention, unless otherwise indicated, for each reactor in the series a gas stream inlet temperature of 710°F is used and the gas composition for feed thereto is chosen to provide for a  $\Delta T_R$  of 75°F for



-27-

an outlet gas of 785°F at an outlet pressure that provides for a partial pressure of steam of approximately 2 ata. The methoxy feed for each is MeOH, DME, or a mixture thereof as indicated and is as available for use at a temperature of 100°F. The diluent recycle gas is a C<sub>2</sub>- and C<sub>3+</sub> gaseous hydrocarbon product of the MTG process or a mixture thereof in a molar ratio that provides a lb-mole quantity thereof to have a specific heat content as indicated. Further, specific heat values of the various components of the involved gas streams are utilized for calculations of the specific heat contents of these gas streams as given in the text which follows. The precise numerical values of these specific heat values may vary somewhat in actual practice with variations in the precise compositions of the components and/or the temperature and pressures to which they are actually subjected, as will be appreciated by those skilled in the art. As desired, in putting this invention into actual practice, one skilled in the art may without undue experimentation determine more precise and accurate numerical values for the circumstances of the actual application. Nevertheless, this would but slightly alter the precise numerical values given hereafter in the discussion of results of the use of this invention, but will not significantly affect the general conclusions discussed about the results and benefits to be had from a practice of this invention.

#### The Fresh Feed Composition

The composition of fresh feed to be added to a product effluent gas from a preceding MTG reaction to form a combined gas to be fed to a succeeding MTG reaction may be conceptually viewed as comprising two components which in sum equal the fresh feed composition. The first component of the fresh feed is that amount of alkoxy compound that is required to heat up the product effluent gas composition by the delta ( $\Delta$ ) between  $T_R$  and  $T_I$  ( $\Delta T_R$ ) desired to be achieved in the succeeding MTG reaction. The second component is that quantity of alkoxy plus recycle diluent composition

-28-

which by itself would react with a  $\Delta T_R$  desired for the succeeding MTG reaction (hereafter this component is referred to as the " $\Delta T_R$  balanced alkoxy-recycle diluent composition"). When summed, the first and second  
5 components provide for a total fresh feed having a total specific heat content that will cool down the effluent gas by heating up the fresh feed to form a combined gas of the temperature desired as the inlet temperature ( $T_I$ ) for admission to the succeeding MTG reaction. This in turn  
10 then dictates the temperature to which the fresh feed must itself be preheated ( $T_p$ ) before being mixed with the product effluent gas which is at its reaction temperature ( $T_R$ ) to form the combined gas at temperature  $T_I$  that upon reaction in a succeeding MTG zone will increase in  
15 temperature by  $\Delta T_R$  to yield a new effluent gas of an outlet temperature as desired,  $T_R$ .

Wherein one has two gas streams, each being at the same temperature, say  $T_R$ , then upon mixture of one with the  
20 other a combined gas stream of the same temperature  $T_R$  is obtained. However, if one takes one gas stream that has already reacted its alkoxy content to reach a temperature of  $T_R$  and another gas stream which is at a temperature  $T_p$  from which by reaction of its alkoxy content would reach a  
25 temperature of  $T_R$  and mix the hot with the cooler gas stream a combined gas stream is obtained having a temperature  $T_I$  which is less than the  $T_R$  of the hot gas stream but greater than  $T_p$  of the cooler gas stream. Thereafter the reaction of the alkoxy content of this  
30 combined gas stream will elevate its temperature to  $T_R$ ; this because each of the component parts of this combined gas stream -- the hot and the cooler gas streams -- were either once at the temperature  $T_R$  or by reaction of its alkoxy content would be elevated to the temperature  $T_R$ .  
35 The temperature  $T_I$  that is obtained upon mixing of the two gas streams is related to the specific heat content of each, which in turn is related to the composition and

-29-

quantity of each. Each molecular species comprising either gas stream has a specific heat value in terms of the heat (BTU) required to elevate its temperature ( $^{\circ}\text{F}$ ) per a unit quantity (lb-mole) of that species. Herein, specific heat values are given in terms of BTU/ $^{\circ}\text{F}$ /lb-mole, meaning the number of BTUs required to elevate one lb-mole of that material by one  $^{\circ}\text{F}$ . The specific heat content of a gas stream is then the number of BTUs required to elevate that gas stream by one  $^{\circ}\text{F}$ , and this specific heat content is the sum of the specific heat value of a species times its quantity for each species contained in the gas stream.

Thus, for example, for methanol ( $Q_R = 24,000$  BTU/lb-mole) to condition it for reaction to hydrocarbon products such that the temperature increase due to its reaction is  $75^{\circ}\text{F}$  ( $\Delta T_R$ ) requires that the specific heat content of the feed gas containing this one lb-mole of methanol be  $24,000/75 = 320$  BTU/ $^{\circ}\text{F}$ . The one lb-mole of methanol itself contributes 16.94 BTU/ $^{\circ}\text{F}$  of this specific heat content, leaving 303.06 BTU/ $^{\circ}\text{F}$  of this content to be satisfied by other components, namely the diluent recycle gas comprising  $\text{C}_2$ -,  $\text{C}_3$ +, steam, hydrogen or mixtures thereof. For discussion purposes the following specific heat values for such recycle components are assumed;  $\text{C}_2$ - hydrocarbon gas, 13.16 lb BTU/ $^{\circ}\text{F}$ /lb-mole;  $\text{C}_3$ + hydrocarbon gas, 36.0 BTU/ $^{\circ}\text{F}$ /lb-mole; steam, 8.8 BTU/ $^{\circ}\text{F}$ /lb-mole; hydrogen, 8.0 BTU/ $^{\circ}\text{F}$ /lb-mole. Selecting a 3:1 molar ratio of  $\text{C}_2$ :- $\text{C}_3$ + hydrocarbon gas as the diluent, this recycle mixture has a specific heat value of  $[(3 \times 13.16) + (36.0)]/4 = 18.87$  BTU/ $^{\circ}\text{F}$ /lb-mole. Then 16.0604 lb-moles of this 3/1 recycle diluent gas would be required for each 1 lb-mole of methanol to form a feed gas that would react with a temperature increase of  $75^{\circ}\text{F}$ . This  $\Delta T_R = 75^{\circ}\text{F}$  balanced gas composition would then be:

$\text{CH}_3\text{OH} = 1.00$  lb-mole,

Recycle (3/1) = 16.064 lb-mole,

Specific Heat Content = 320 BTU/ $^{\circ}\text{F}$ .

This feed as first preheated to  $710^{\circ}\text{F}$  when contacted with an MTG catalyst will react to form a product gas having a

-30-

temperature of 785° and a specific heat content which, for discussion purposes, is assumed to be the same as the feed gas from which it was formed, namely 320 BTU/°F.

5 This hot product gas at 785°F has a content of heat in excess of that at which it would otherwise have a temperature of 710°F of 24,000 BTU, which is the heat released by reaction of the methanol from which the product gas stream was formed. Transfer of this 24,000 BTU of heat from this product gas stream to another medium will reduce  
10 the temperature of this product gas stream from its 785°F temperature to a temperature of 710°F. The medium of transfer can be a cooler gas stream, and the transfer can be accomplished by indirect exchange as through the heat transfer surfaces of an adiabatic heat exchanger or by  
15 direct gas-to-gas contact by admixture of the two gases.

In this invention the transfer of this excess product heat to the cooler feed gases is in part accomplished through adiabatic heat exchangers -- to preheat a fresh feed gas charges to a temperature  $T_p$  -- and in part by  
20 direct gas-to-gas contact -- to finally warm up the preheated fresh feed gas charges from its  $T_p$  preheat temperature to a temperature  $T_1$  desired for contacting it with a MTG catalyst. The direct gas-to-gas heat exchange is first accomplished, and the product gas from the last of  
25 the MTG reactions in series is used for indirect heat exchange through adiabatic heat exchangers to warm up the fresh feed gases to their preheat  $T_p$  temperature.

As to the direct gas-to-gas heat exchange to warm up a fresh feed gas from its preheat temperature  $T_p$  to the  $T_1$   
30 temperature desired for its contact with an MTG catalyst, the specific heat content of the fresh feed gas governs how much it can be warmed up by the cooling down from  $T_R$  of the hot product gas with which it is mixed to a temperature  $T_1$ . The amount by which the fresh feed gas will be warmed  
35 up ( $T_1 - T_p$ ), while the product gas is cooled down ( $T_R - T_1$ ) is related to the ratio of the specific heat content of the

-31-

fresh feed gas ( $S_f$ ) to the specific heat content of the product gas ( $S_p$ ) according to the equation:

$$S_f = \frac{(T_R - T_I)}{(T_I - T_P)} \times (S_p).$$

For the case under discussion, wherein it is desired to have the next reaction begin at a temperature of  $T_I = 710^\circ\text{F}$ , the composition and quantity of the new feed gas are governed then by

$$S_f (710 - T_P) = 24,000,$$

and its specific heat content is a function of the temperature to which it is preheated before admixture with the hot product gas. Selecting then, for discussion purposes, a feed gas preheat temperature of  $635^\circ\text{F}$  ( $T_P$ ), the specific heat content of the fresh feed must equal that of the product gas with which it is to be mixed, and the combined gas stream will have a specific heat content that is the sum of its component parts. To then have this combined gas stream react to a new product gas temperature  $T_R = 785^\circ\text{F}$  requires that it contain a quantity of alkoxy compound, here for discussion purposes, methanol, to heat its now doubled specific heat content of  $640 \text{ BTU}/^\circ\text{F}$  by  $75^\circ\text{F}$ , or  $640 \times 75 = 48,000 \text{ BTU}$ . This quantity of heat is supplied through the reaction of 2 lb-moles of methanol ( $Q_R = 24,000 \text{ BTU/lb-mole}$ ) which contributes  $33.88 \text{ BTU}/^\circ\text{F}$  towards the needed  $320 \text{ BTU}/^\circ\text{F}$  specific heat content required for the new feed gas, leaving  $286.12 \text{ BTU}/^\circ\text{F}$  of the heat content to be supplied by diluent gas. Where this remaining quantity is supplied by a diluent gas comprising a 3/1 molar ratio of  $\text{C}_2:\text{C}_3$  hydrocarbon gas, then  $15.1627 \text{ lb-moles}$  of such recycle gas is required. Hence the composition of the fresh feed gas would be:

$$\text{CH}_3\text{OH} = 2.00 \text{ lb-mole},$$

-32-

Recycle (3/1) = 15.1627 lb-mole,  
Specific Heat Content = 320 BTU/°F

Reaction of the combined gas mixture will then produce a  
new product gas having a temperature of 785°F and a  
5 specific heat content of 640 BTU/°F.

This new product gas ( $T_R=785^\circ\text{F}$ ;  $S_p=640$  BTU/°F) may be  
used as the hot gas source for mixture with a new portion  
of fresh feed gas to form a combined gas mixture for  
another reaction over an MTG catalyst between any reaction  
10 temperature zone of  $T_i$  to  $T_R$  as may be desired.

Take for instance that for this next reaction it is  
desired to contact the next MTG catalyst at a temperature  
 $T_i = 700^\circ\text{F}$  and have a new product gas temperature from that  
reaction limited to  $740^\circ\text{F}$ . In this case the previous  
15 product gas requires cool down from  $785^\circ\text{F}$  to  $700^\circ\text{F}$  for a  $T_R$   
-  $T_i$  of  $85^\circ\text{F}$ , meaning the previous product gas must give up  
 $640$  BTU/°F  $\times$   $85^\circ\text{F} = 54,400$  BTU of heat which is then  
available for warm up of the new feed gas to the desired  
inlet temperature of  $700^\circ\text{F}$ . Once this previous product gas  
20 component has been cooled to  $700^\circ\text{F}$ , at its specific heat  
content of  $640$  BTU/°F, to increase its temperature to the  $T_R$   
 $= 740^\circ\text{F}$  desired for the new product gas requires  $640$  BTU/°F  
 $\times$   $40^\circ\text{F} = 25,600$  BTU of heat to be released by reaction of  
methanol contained in the new feed charge. To this end,  
25 after reaction by methanol has warmed itself or its  
reaction product up by  $40^\circ\text{F}$  to consume  $16.94 \times 40 = 677.6$   
BTU of the heat of its reaction, there remains  $24,000 -$   
 $677.6 = 23,322.4$  BTUs of heat to warm up the previous  
product gas, thus  $25,600/23,322.4 = 1.06667$  lb-mole  
30 methanol are required to reheat the previous product gas  
from  $700$  to  $740^\circ\text{F}$ . If again the new feed gas has been  
preheated to a  $T_p$  temperature of  $635^\circ\text{F}$  the composition and  
quantity of the new feed gas is governed by

$$S_p (700 - 635) = 54,500$$

35 or its  $S_p$  required is  $836.923$  BTU/°F of which  $18.594$  BTU/°F  
is provided by the methanol required to reheat the previous  
product gas that will become part of the combined gas

-33-

stream to be reacted. Hence, 818.329 BTU/°F of value remains to be filled in the new feed gas by methanol and recycle constituents and these constituents must react from a  $T_1$  temperature of 700°F to the new temperature desired of 740°F. Here, to moderate the reaction of one lb-mole methanol to a 40°F increase in temperature upon its reaction requires a specific heat content of  $24,000/40 = 600$  BTU/°F, of which that one-lb-mole of methanol contributes 16.94 BTU/°F, leaving 583.06 BTU/°F of content to be supplied by a recycle diluent gas. Again, using a 3/1  $C_2:C_3$  recycle gas diluent would require 30.8988 lb-mole of such diluent. Hence, the  $\Delta T_R = 40^\circ\text{F}$  balanced gas composition would be:

CH<sub>3</sub>OH - 1.00 lb-mole,

Recycle (3/1) - 30.8988 lb-mole

Specific Heat = 600.0 BTU/°F.

To supply the 818.329 BTU/°F needed, 1.36388 times this quantity of the  $\Delta T_R = 40^\circ\text{F}$  balanced gas composition is needed. Hence the new feed gas would be:

	Component To Reheat Previous Product Gas	$\Delta T_R = 40^\circ\text{F}$ Balanced Composition x 1.36388	New Feed Gas
CH <sub>3</sub> OH	1.097657	1.36388	2.461538
Recycle	-0-	42.14231	42.14231
Specific Heat Content	18.594	818.329	836.923

It should be clear from the general discussion given above that in order for the new process to effect significant savings in heat exchange the above mentioned  $T_p$  temperature of the added feed should be significantly lower than the  $T_1$  temperature of inlet to the reactor obtained after addition of the hot exit gas from the earlier reactor. The given examples clearly demonstrate that a reduction of about a factor of 2 can be obtained with as little as 60°F difference between these two temperatures. It is, however, preferred to use a more optimal temperature

-34-

difference of about 200°F and a larger number of reactors, like 10, preferably 5 to 8, so that a more sizeable heat exchange duty reduction of about one order of magnitude can be obtained, especially when using DME only.

5        It should be understood that especially when using a larger number of reactors, the resulting pressure drop may begin to exert a negative effect on the size of the heat exchanger. This has been taken into account in calculation of the advantages to be obtained.

10        Accordingly, to maximize the efficiency of heat exchange operations (which is a variable of pressure and the volume of gas treated for heat exchange) while also maximizing the saving required for fresh feed preheating and/or product gas cooldown for product recovery the  
15        following conditions are preferred:

- 20        (1) preheating of the fresh feed gas to a temperature within 75 to 260°F of the  $T_i$  temperature selected for admission of the combined gas stream to the succeeding MTG reaction zone, preferably to within 100 to 210°F, and more preferably to within 100 to 160°F;
- 25        (2) formation of the combined gas stream to have a temperature  $T_i$  from 650-720°F, and preferably from about 675-720°F;
- 30        (3) selection of the alkoxy content of the fresh feed stream to have a heat of reaction content that, upon reaction of that alkoxy content thereof, would increase the temperature of the combined gas stream by a  $\Delta T_R$  of 10-150°F, preferably by 30-120°F, more preferably by 50-100°F and most preferably by 50-85°F; and
- 35        (4) formation from reaction of the combined gas stream in the succeeding MTG reaction zone of a new effluent gas having a temperature  $T_R$  of from about 700 to 800°F, preferably from about 730 to 800°F, and more preferably of from about 750 to 785°F.



-35-

Reactor Sequence

Figure 1 illustrates one embodiment of the process which employs five MTG reactors in series flow, reactors 10, 20, 30, 40 and 50. A methoxy feed with an appropriate amount of water to allow initiation of reaction over the MTG catalyst together with an appropriate amount of recycle diluent gas at 100°F, is fed by line 2 to heat exchange 3 and is there preheated to 710°F then fed by line 4 to the inlet of reactor 10 and passed into contact with an MTG catalyst. The product effluent gas is passed by line 11 to line 12. A fresh quantity of methoxy feed at 100°F passes from line 5 through heat exchanger 6 and is preheated to a temperature  $T_p$  and then passed by line 7 through metering valve 7a into admixture with the product effluent gas in line 12. A further quantity of recycle diluent gas 5a at 100°F passes through heat exchanger 8 and is preheated to temperature  $T_p$  then passed by line 9 through metering valve 9a into admixture with the product effluent gas and methoxy feed in line 12. The combined gas stream passes from line 12 into contact with the MTG catalyst in reactor 20 and the product effluent gases pass therefrom by line 13 into line 14 where the product effluent gas becomes admixed with a further quantity of methoxy feed and recycle diluent gas, each at temperature  $T_p$ , as metered into line 14 through valves 7b and 9b respectively. Again, the product effluent gas from reactor 30 passes by line 15 into a further quantity of methoxy and recycle gases each at  $T_p$  as metered in through valves 7c and 9c respectfully, and the combined gases pass by line 16 into contact with an MTG catalyst in reactor 40. The product effluent gas from reactor 40 passes by line 17 into mixture with a further quantity of methoxy and recycle diluent gas at  $T_p$  as metered in through valves 7d and 9d respectively and the combined gases pass by line 18 into contact with an MTG catalyst in reactor 50. The product effluent gas from reactor 50 passes by line 19 to subsequent processing units where it is cooled to 100°F for separation and recovery of its various components, such

-36-

as its C<sub>2</sub>-and C<sub>3</sub>+ hydrocarbon content for recycle use as a diluent gas, its liquid hydrocarbon content to be processed into its fuel grade fractions, and its water content.

Heat Exchange Requirements

5           In the process of converting an alkoxy compound to hydrocarbon products by contact with an MTG catalyst it is necessary to heat up feedstocks of alkoxy-diluent gases from their unit available temperature ( $T_0$ ) to a temperature at which they will react over an MTG catalyst, namely  $T_1$ .  
10       By reason of the exothermic reaction of the alkoxy compound to hydrocarbon product the product effluent gas resulting from contact with an MTG catalyst has an even higher temperature,  $T_R$ . To recover the hydrocarbon product from the reaction gases, it is necessary to cool the product  
15       effluent gas from its temperature  $T_R$  to a temperature at which its normally liquid hydrocarbon content condenses, typically about 100°F.

          Typically, the product gases at  $T_R$  and feedstock gases at  $T_0$  are passed through adiabatic heat exchangers wherein  
20       heat content  $Q$  is exchanged between the product gases and feedstock gases through a heat exchange surface that separates these gas streams, whereby the product gases cool down in temperature to the extent they transfer a content  $Q$  of their heat to the feedstock gases which are thereby  
25       increased in temperature.

          In an ideal case, the product gas contains a quantity of heat  $Q$  that is in excess of that quantity required to heat up the feedstock gases to  $T_P$  by an amount that is equal to the heat released by the alkoxy compound that  
30       reacted to form the product gases. Thus, following the first heat exchange between the product gases at  $T_R$  and feedstock gases at  $T_0$  through the heat exchange surface of an adiabatic heat exchanger, the feedstock gases are heated up to  $T_P$  and the reaction gases are cooled down to a  
35       temperature  $T_x = T_R - (T_P - T_0)$ . Hence, to recover normally liquid hydrocarbon compounds from the reaction gases it is necessary to cool them further from their  $T_x$  temperature to

-37-

about 100°F, which is typically the temperature  $T_0$  at which the feedstock gases are available since a major portion of the feedstock gases are the  $C_2$ -and/or  $C_3$ + hydrocarbon by-products recovered from the reaction gases and used as the recycle or diluent component of a feedstock. In this last step of reaction gas cooling, the reaction gases at  $T_r$  are heat exchanged in an adiabatic heat exchanger operating with chill water, typically at a chill water temperature of 70°F.

With the process of this invention it is possible to realize significant economies in the heat exchange requirements in terms of the size of the heat exchangers required for feedstock heatup duties and the heat exchangers required for the final step of reaction gas cooldown for hydrocarbon product recovery.

For example, on the basis of methoxy equivalent processed to hydrocarbon product, using as the standard for comparison a process comprising a single reactor pass of the same quantity of methoxy compound for conversion to hydrocarbon product at a reactor inlet temperature of 710°F, and outlet temperature of 785°F and at an outlet pressure that provides for a partial pressure of water of 2.15 ata and wherein the feedstock gases are available at 100°F and the recycle diluent gas comprises a 1:3 molar ratio of  $C_3$ +: $C_2$ -hydrocarbon by-product gas, Figures 2 and 3 illustrates the affect on the size of the heat exchangers based upon the relative heat exchange surface area ( $A_R$ ) required for feedstock heating.

Figure 3 is for methanol containing 0.35 moles water per mole of methanol as feed, Figure 2 is for dry DME as feed.

Figures 2 and 3 indicate the results of a series of calculations based on assuming the maximum allowable pressure in the second reactor, reactor II, which is the first reactor with a low amount diluent recycle gas in the feed. From then on a pressure drop per reactor stage of 0.35 ata is taken. The final pressure out of the last

-38-

reactor is taken as guidance for the size of the relative heat exchanger surface area necessary for warmup of the feeds. The heat exchanger for the feed of the first reactor, reactor I, is separately sized from the combined heat exchanger for the combined cold feed. For all  
5 reactors in both cases a temperature of reaction is chosen, starting at 710 and ending at 785F. The added feed is fed in at a series of preheat temperatures  $T_p$ , varying in steps of 50°F from 100 to 650°F. The figures clearly show a  
10 minimum for the relative heat exchange surface area, that varies with the number of reactor steps used. The minimum seems to be at about the same temperature independent of the nature of the methoxy feed. For both feeds considered, the minimum is at a preheat temperature  $T_p$  of about 550°F  
15 for five reactors and slowly decreases to about a rather flat minimum at  $T_p = 450^\circ\text{F}$  with the use of ten stages.

For comparison it should be noted that a one reactor approach as applied to methanol with 0.35 mole of water per mole of methanol requires a heat exchange surface area of  
20 about 325.4 relative units on the basis of a pressure of operation of 22.06 ata resulting from the chosen feed. With the same feed the present system with ten stages reduces this heat exchange surface area number to 42.6 relative units while use of DME reduces it further down to  
25 28.5 relative units.

The conclusion is therefore that the process of this invention reduces the required heat exchange surface area for feed gas warm-up between 8 and 10 fold.

As may also be realized, in the process of this  
30 invention the use of a recycle diluent gas of a low specific heat content as a feedstock component is preferred to that of a diluent gas of a high specific heat content. As the  $C_2$ - content of a diluent recycle gas increases at the expense of its  $C_3$ - content while the specific heat  
35 content of the diluent gas remains the same, then the quantity of diluent recycle gas increases and constitutes a larger volume of the final product gas. This in turn

-39-

means that the water by-product content of the final product gas becomes a small fraction of the total gas content and the gas can be processed at a higher pressure while still maintaining its water content at the same steam partial pressure. For example, where MPH means mole-per-hour, to react 1 MPH methanol ( $\text{CH}_3\text{OH}$ ) to a hydrocarbon product with a temperature rise of the gas stream limited to 75°F requires a feed gas composition having a specific heat content of 320 BTU/°F. Of this amount the methanol itself contributes 16.94 BTU/°F leaving 303.06 BTU/°F to be supplied by a diluent recycle gas. If supplied solely by a  $\text{C}_{3+}$  recycle gas then 8.42 MPH  $\text{C}_{3+}$  recycle would be required and the final product gas would comprise 8.42  $\text{C}_{3+}$  recycle, 1 MPH  $\text{H}_2\text{O}$ , and 0.1724 MPH hydrocarbon product and a total pressure of 19.18 ata would produce a steam partial pressure of 2.0 ata. On the other hand, if the remainder of the specific heat content required were supplied solely by a  $\text{C}_2$ - recycle then 23.03 MPH  $\text{C}_2$ - recycle would be required and the final product gas would comprise 23.03 MPH  $\text{C}_2$  recycle, 1 MPH  $\text{H}_2\text{O}$  and 0.1724 MPH hydrocarbon product. At a pressure of 48.40 ata such gas composition would have a steam partial pressure of 2.0 ata. Of the two gas compositions discussed, that using the  $\text{C}_2$ - recycle is more efficiently heat exchanged because of its processing at the higher pressure, in relative terms, requiring only about 57.4% of the heat exchange surface area as would otherwise be required by the gas composition using a  $\text{C}_{3+}$  recycle. However, the  $\text{C}_{3+}$  hydrocarbon by-product steam contains olefins and use of a  $\text{C}_{3+}$  recycle promotes further reaction of the olefin content thereof to  $\text{C}_{3+}$  hydrocarbons, increasing the yield of the gasoline grade hydrocarbon product. Hence, a reasonable amount of  $\text{C}_{3+}$  content in the diluent recycle gas is generally desirable. Accordingly, use of the  $\text{C}_2$ - hydrocarbon by-product (specific heat about 13.16 BTU/°F/lb-mole) and diluent gases rich in  $\text{C}_2$ -compared to  $\text{C}_{3+}$  hydrocarbon by-product, on the order of a  $\text{C}_2$ :- $\text{C}_{3+}$

-40-

molar ratio of from about 3:1 to about 1:3, as the diluent gas component of a feedstock is preferred.

The preference with respect to the number of reactors in a series and the fresh alkoxy recycle diluent feed preheat temperature are somewhat interrelated. Given the fact that to maintain gas flow through the reaction train a pressure drop must be allowed across each reactor, the number of reactors in a series at which a maximum savings in heat exchange duties per methoxy equivalent converted is limited by this pressure drop factor since lower pressure means lower heat exchange efficiency.

Generally, the maximum in heat exchange economies are realized in the range of fresh feed preheating of about  $T_p = 400$  to  $550^\circ\text{F}$ . Within this range the number of MTG reactors required to realize the maximum in heat exchange required may vary from about 5 to about 10 reactors. In a five reactor series the maximum in heat exchange economy is realized with a preheat of the fresh feeds to about  $550^\circ\text{F}$ ; whereas with a fresh feed preheat to  $500^\circ\text{F}$ , the maximum in heat exchange economy is realized in the last of a series of six to eight reactors; and at a preheat of  $450^\circ\text{F}$  the maximum economy is realized in the last of a series of nine to ten reactors. On the basis of total methoxy equivalent converted, compared to the relative heat exchange surface area required for feed gas warm-up for conversion in a single reactor pass; in accordance with this invention with a fresh feed gas preheat of  $550^\circ\text{F}$  with a five reactor series requires only about 26.8% of the heat exchange surface area; for a series of six to eight reactions with a fresh feed preheat to  $500^\circ\text{F}$  only 22.1 to 16.3% of the heat exchange surface area is, respectively, required; and for a series of nine to ten reactors with a preheat of 450 only 14.5 to 13.1% of the heat exchange surface area is required.

#### Product Compositional Control

For purposes of influencing the hydrocarbon distribution of the product in favorable ways, it is

-41-

possible with the process of this invention to tailor the conditions of inlet-outlet temperature and effluent gas steam partial pressure of water for any reactor in the series to a set of conditions different than other reactors in the series. For example, durene (1,2,4,5 tetramethyl benzene) is not a desirable hydrocarbon component of the product whereas toluene and xylene ("TX" octane boosters) are desirable hydrocarbon components. To minimize the durene and maximize the TX components of the hydrocarbon product, it may be desirable to operate the early reactors in the series at a higher inlet temperature condition (i.e.  $T_i \geq 720^\circ\text{F}$ ) to decrease aromatic hydrocarbon production therein while operating the last reactor(s) at a lower inlet-outlet temperature condition (i.e.,  $T_i = 700$ ,  $T_R \geq 760^\circ\text{F}$ ) to increase aromatic production, but limit or reduce over methylation of the aromatics to durene and/or trimethyl benzene, providing all reactors are operated at a similar partial pressure of water outlet value.

#### The Recycle Diluent Gas Hydrogen Content

As mentioned before, heat exchangers operate more efficiently at higher rather than lower pressures. As a rule of thumb heat exchange is enhanced by the factor of pressure (P) to the power 0.6. The relative surface area needed therefor is related to pressure by the factor  $(1/P)^{0.6}$ . Further, with respect to the heat exchange of gases, exchange is more efficient as to species of lower molecular weight than of higher molecular weight. Hence to further enhance the efficiency of heat exchange operations it is preferred to utilize as a diluent gas composition one which incorporates a percentage of hydrogen (specific heat about 8 BTU/°F/lb-mole) ranging from about 10 to about 50 mole% hydrogen and more preferably from about 15 to about 30 mole % hydrogen.

#### First Reactor Recycle Operation

In another embodiment of the invention the heat exchange duties required for conversion of alkoxyl compound to methanol may be even further reduced by operating the

-42-

first MTG reactor in a mode wherein a portion of its produce effluent gas is recycled back to its inlet for combination with fresh alkoxy-diluent recycle feedstock admitted thereto.

5           This mode is illustrated in Figure 4, wherein feed gas preheated to a temperature  $T_p$  is routed by line 70 to the inlet 72 of MTG reactor 74. Product gas at a temperature  $T_R$  is taken from reactor 74 by line 76 and is then split into two product streams, one of which proceeds through  
10   line 80 to the next MTG reactor in the series (not shown) and the other product gas portion is routed by line 78 to a hot gas fan 82 wherein it is recompressed to a pressure equal to that of the feed gas to MTG reactor 74 and then routed by line 84 for addition to reactor inlet 72 in  
15   admixture with feed gas routed to the inlet 72 via line 70. In this mode, as illustrated by Figure 4, the alkoxy-diluent recycle feedstock would be preheated to a preheat temperature  $T_p$  and upon combination with the recycle portion of the product stream at  $T_R$  would form a combined  
20   gas stream of temperature  $T_i$  for contact with the MTG catalyst. In this mode of operation the composition of the alkoxy-diluent recycle feedstock is adjusted to provide an amount of alkoxy compound relative to the diluent recycle content of this feed that upon reaction to hydrocarbon  
25   product provides a heat of reaction that raises the temperature of the combined gas stream from  $T_i$  to  $T_R$ . Otherwise stated, the quantity of alkoxy compound relative to the diluent recycle content of the feed is that which by heat of reaction would increase the temperature of the feed  
30   alone from its preheat temperature  $T_p$  to  $T_R$ .

          This product recycle mode of operation for the first MTG reactor means that preheating of the feedstock gases can more efficiently be accomplished, i.e., a smaller heat exchange area is required, because the differential heat  
35   exchange temperature  $\Delta T$  as reflected in the heat exchange factor  $(1/\Delta T)$  is now



-43-

$T_R - T_P$  rather than  $T_R - T_I$ . To accomplish this product recycle requires a slight recompression of this portion of the product gas from its reactor outlet pressure ( $P_0$ ) to the gas pressure required for the reactor inlet ( $P_I$ ), in other words, to compensate for the pressure drop occurring across this reactor. This may readily be accomplished with a hot fan, a conventional item of equipment. However to utilize a conventional hot fan for this recompression, the volume of product recycle that can be accomplished is limited by the fan capacity and this in turn will generally set the preference for the conditions to be employed in the subsequent MTG reactors in the series. That is, for a given total of gasoline production desired, once the capacity of the first reactor product recycle is determined, the most optimum of conditions for subsequent feed preheat temperature and the number of MTG reactors may be selected for the balance of the desired gasoline production.

#### EXAMPLES

The following examples illustrate operations in accordance with the process of the invention and, in some cases, for comparison purposes illustrate operations in accordance with prior art practice. Unless otherwise indicated the following values were applied in preparation of the examples.

#### Heat of Reaction

- (1) Dimethylether (DME)  $\rightarrow$  (2/5.8) hydrocarbons +  $H_2O$   
(35,200 BTT/lb-mole DME)
- (2) Methanol (MeOH)  $\rightarrow$  (1/5.8) hydrocarbons +  $H_2O$  (24,000  
BTU/lb-mole MeOH)

-44-

	<u>Specific Heats</u>	<u>BTU/°F/lb-mole</u>
(1)	DME	25.08
(2)	MeOH	16.94
(3)	H <sub>2</sub> O	8.8
5 (4)	C <sub>2</sub> - recycle gas	13.16
(5)	C <sub>3+</sub> recycle gas	36.0
(6)	Hydrocarbon Product	47.212
(7)	H <sub>2</sub>	8.0

10 Operations in accordance with the proposed invention  
in comparison to that for a single reactor pass method of  
converting the same quantity of methoxy equivalent is  
discussed below. In each of Example 1 to 5, unless  
otherwise indicated, the effluent gas temperature at the  
15 outlet (T<sub>R</sub>) of each MTG reactor is 785°F, the inlet gas  
temperature (T<sub>I</sub>) of the gas feeds to each MTG reactor is  
710°F, and the partial pressure of steam in the effluent gas  
of each MTG reactor is 2.15 ata. A pressure drop of 0.35  
ata across each MTG reactor is assumed. Example 1 is a  
20 comparative example and illustrates the conversion of the  
methoxy component of the feed gas by a single pass through  
one reactor. Examples 2 to 5 illustrate the conversion of  
a similar quantity of methoxy component in a series of five  
MTG reactors operating in accordance with the process of  
25 this invention. The relative heat exchange surface area  
(A<sub>R</sub>) required for feed gas warm-up in the examples is  
calculated according to the relationship:

$$A_R = Q (1/\Delta T) (1/P)^{0.6}$$

wherein Q is the quantity of heat required to warm-up a  
30 feed gas from temperature T<sub>0</sub> to T<sub>P</sub>, with T<sub>0</sub> = 100°F for all  
examples; the ΔT is T<sub>R</sub>-T<sub>P</sub> with T<sub>R</sub> = 785°F for all examples;  
and P is the pressure of the last reactor effluent gas and  
is that pressure in atmospheres absolute (ata) that  
provides for a partial pressure of steam in the effluent  
35 gas of 2.15 ata.

Example 1 (Comparative):

-45-

This example illustrates a single pass conversion of methoxy compound, like that of the single pass process scheme employed in New Zealand. Three situations are presented: (a) wherein the methoxy component is methanol and water in a 1 to 0.35 mole ratio, (b) wherein the methoxy component is an equilibrium mixture made from the methanol-water composition above, and contains methanol, dimethyl ether and water; and (c) wherein the methoxy component is dry dimethyl ether. The recycle diluent gas for each situation comprises a mixture of C<sub>2</sub>- and C<sub>3</sub>+ hydrocarbon by-product gases wherein the molar ratio of C<sub>2</sub>:C<sub>3</sub>+ is 3:1. Quantities are given in lb-moles/hour which is denoted as MPH.

Feed MPH	(a) MeOH + H <sub>2</sub> O	(b) Equilibrium Mix MeOH + DME	(c) Dry DME
MeOH	28,706	7,078	—
DME	—	10,814	14,353
H <sub>2</sub> O	10037.1	20,851.1	—
C <sub>2</sub> -	342,123.3	269,194.0	253,255.5
C <sub>3</sub> +	114,041.1	89,731.3	84,451.8
Ar	10.173x10 <sup>6</sup>	9.268x10 <sup>6</sup>	5.031x10 <sup>6</sup>
Final P. (ata)	27.7385	22.342	53.4792

If instead of a recycle gas having a C<sub>2</sub>:C<sub>3</sub>+ Mole ratio of 3:1 a recycle gas having a 5:1 ratio were used (which is similar to the actual New Zealand recycle gas) then the relative heat exchange surface area required for the three situations would then be: (a) 9.596 x 10<sup>6</sup>; (b) 8.735 x 10<sup>6</sup>; and (c) 4.74 x 10<sup>6</sup>. It should be noted that with respect to the use of dry DME for a single pass conversion, that the high pressure of greater than 50 ata be viewed as

-46-

undesirable in that it may promote the production of such a heavy hydrocarbon product as to cause fast cokeing, hence inactivation, of the MTG catalyst. Hence the possible attainment of greater heat exchange economies due to such high pressure operations may be illusory.

Example 2

An equilibrium mixture of 7,078 MPH  $\text{CH}_3\text{OH}$ , 10,814 MPH DME and 20,851 MPH  $\text{H}_2\text{O}$  is processed in accordance with the invention in a series of five MTG reactors. For the first MTG reactor of the series a portion of this methoxy content, together with an appropriate amount of  $\text{C}_2$ - and  $\text{C}_3$ - recycle gas of a  $\text{C}_2$ :- $\text{C}_3$ + ratio of 3:1 and a quantity of water to provide for a reactor outlet steam pressure of 2.15 ata is preheated to 710°F, the remainder of this methoxy content is combined with the  $\text{C}_2$ - and  $\text{C}_3$ - recycle gas of 3:1 mole ratio and preheated to the  $T_p$  temperature indicated and proportioned as fresh feed to the four subsequent MTG reactors wherein each portion is combined with the effluent gas from a preceding MTG reactor before being fed to its succeeding MTG reactor. The relative heat exchanger surface areas required for preheating the feed to the first reactor, Reactor I, and for preheating the feeds for the subsequent four reactors, Reactors II-V, are given below, as is the total of the relative heat exchange surface area required.

$T_p$ : Temperature (°F) Fresh Feed Preheat for Reactors II-V	Final Product Gas Pressure, (ata)	Relative $A_{RI}$ : Heat Exchange Surface Area, Reactor I, ( $\times 10^6$ )	Relative $A_{II-V}$ : Heat Exchange Surface Area, Reactors II-V ( $\times 10^6$ )	Total Heat Exchange Surface Area ( $\times 10^6$ )
650	11.6	0.304	3.746	4.050
600	8.6	0.902	2.098	3.000
550	7.2	1.472	1.266	2.739
500	6.1	2.006	0.828	2.834
450	5.4	2.463	0.556	3.018

-47-

400	4.8	2.893	0.382	3.276
-----	-----	-------	-------	-------

The above data demonstrates that as the fresh feed gas preheat temperature  $T_p$  is lowered, meaning that the relative proportion of the fresh feed being mixed with the hot effluent gas from a preceding reactor becomes smaller, that the contribution of the heat exchange duty requirements for preheating the first reactor feed gas to the total heat exchange duties becomes greater. As a consequence, even though of the total methoxy converted that converted in the first reactor is a small fraction, the requirements for its warm-up together with its recycle gas content is of major influence on the total heat exchange area necessary. If instead of a recycle gas having a  $C_2:C_3$  mole ratio of 3:1 a recycle gas having a mole ratio of 1:3 were used, then, using the  $T_p$  condition of 600°F for comparison, the total relative heat exchange surface area required would be  $3.760 \times 10^6$ , this being due to the lower pressure of operation required to maintain the steam partial pressure in the final effluent gas at 2.15 ata.

**Example 3:**

In a manner like that of Example 2, 14,353 MPH dry dimethyl ether is used as the alkoxy component of the feed. The following results are given:

$T_p$ : Temperature (°F) Fresh Feed Preheat for Reactors II-V	Final Product Gas Pressure (ata)	$A_R$ : Relative Heat Exchange Surface Area, Reactor I ( $\times 10^6$ )	$A_R$ II-V: Relative Heat Exchange Surface Area, Reactors II-V ( $\times 10^6$ )	$A_R$ TOTALS: Total Relative Heat Exchange Surface Area ( $\times 10^6$ )
650	28.6	0.162	1.995	2.156
600	20.6	0.489	1.139	1.628
550	16.6	0.818	0.704	1.522
500	13.6	1.137	0.469	1.606
450	12.1	1.391	0.314	1.705
400	9.6	1.869	0.149	2.018

-48-

If instead of a recycle gas having a  $C_2:C_3$  mole ratio of 3:1 a recycle gas having a mole ratio of 1:3 were used, then, using the  $T_p$  condition of 600°F for comparison, the total relative heat exchange surface area required would be  $2.087 \times 10^6$ .

**Example 4:**

The same methoxy feed composition as in Example 2 is utilized under similar conditions except that the first MTG reactor is now operated in a mode wherein a portion of its product gas is recycled back to its inlet and mixed with feed gas thereto. Further, the feed gas to the first MTG reactor is now preheated to either 600°F or 650°F, as indicated below, and by combining it with the portion of product recycle, a combined gas stream of 710°F is formed for inlet to the first reactor.

$T_p$ :		$A_R I$ : Relative Heat Exchange Surface Area, Reactor I	$A_R II-V$ : Relative Heat Exchange Surface Area, Reactors II-V	$A_R TOTAL$ : Total Relative Heat Exchange Surface Area
Reactor Feed Preheat Temp., (°F)	Final Product Gas Pressure (ata)			
I @ 600°F II-V @ 600°F	8.04	$0.289 \times 10^6$	$2.022 \times 10^6$	$2.311 \times 10^6$
I @ 650°F II-V @ 600°F	8.6	$0.433 \times 10^6$	$2.010 \times 10^6$	$2.442 \times 10^6$

**Example 5:**

The same methoxy feed composition as in Example 3 is utilized under similar conditions except that the first MTG reactor is now operated in a mode wherein a portion of its product gas is recycled back to its inlet and mixed with feed gas thereto. Further, the feed gas to the first MTG reactor is now preheated to either 600°F or 650°F, as indicated below, and by combining it with the portion of product recycle, a combined gas stream of 710°F is formed for inlet to the first reactor.

-49-

5	Reactor Feed Preheat Temp., °F	Final Product Gas Pressure (ata)	A <sub>R</sub> I: Relative Heat Exchange Surface Area, Reactor I	A <sub>R</sub> II-V: Relative Heat Exchange Surface Area, Reactors II-V	A <sub>R</sub> TOTALS: Total Relative Heat Exchange Surface Area
10	I @ 600°F II-V @ 600°F	18.6	1.60x10 <sup>6</sup>	1.121x10 <sup>6</sup>	1.281x10 <sup>6</sup>
	I @ 650°F II-V @ 600°F	18.6	0.250x10 <sup>6</sup>	1.160x10 <sup>6</sup>	1.409x10 <sup>6</sup>

By comparison of the data presented in Example 1-5, it is apparent that the process of this invention results in a significant reduction in the heat exchange duties required for feed gas warm-up. Hence, using the equilibrium methanol-DME-H<sub>2</sub>O as the methoxy component of the feed of situation (b) of Example 1 for comparison, even at a lesser than most optimum feed gas preheat of T<sub>p</sub> = 600°F (the optimum being 550°F), as illustrated by Example 2 the same equilibrium methanol-DME-H<sub>2</sub>O component may be converted with only 32% of the heat exchange requirement of Example 1. As illustrated by Example 3, use of a dry DME as the methoxy component of the feed gas in an amount equal in methoxy equivalent to the equilibrium methanol-DME component of Example 1 allows for conversion with only 17.67% of the heat exchange requirement of Example 1. Further as illustrated in Example 3, at the feed gas preheat temperature of 600°F the operational pressure with respect to the dry DME used is 20.6 ata, hence no concern about possible coke over of the MTG catalyst should arise. Further, as illustrated in Example 5, the heat exchange requirements for processing dry DME according to the invention may be further reduced to only about 13% of that required in Example 1 by operating the first MTG reactor in a mode wherein a portion of its effluent gas is recycled back to its inlet to assist in feed gas warm-up.

-50-

Also to be realized in the practice of this invention is a reduction in the heat exchange duties required for the final step of product gas cool-down to recover its liquid hydrocarbon content. Hence, with respect to the product gas resulting in Example 1 from the conversion of the equilibrium mixture of DME-CH<sub>3</sub>OH-H<sub>2</sub>O, the final product gas after heat exchange through an adiabatic heat exchanger to warm feed gas up has a first cooldown temperature around 175°F. By contrast the final product gas resulting from the preheat  $T_p = 600^\circ\text{F}$  process of Example 2 after heat exchange through adiabatic heat exchangers to warm-up feed gas has a first cooldown temperature  $T_x$  around 285°F.

With the process of this invention the final cooldown of the product gas for liquid hydrocarbon recovery requires a smaller heat exchanger because the heat exchanger needed to cool this gas operates with a larger differential temperature,  $\Delta T$ , for the needed cool down.

Although the process of this invention has been described with reference to its preferred embodiment, from this description those skilled in the art may appreciate changes and modifications that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.



-51-

## CLAIMS:

1. A method of making hydrocarbon compounds by contacting an alkoxy compound with an MTG catalyst, comprising the steps of:

combining an effluent gas product from a preceding MTG reaction zone which is at a temperature  $T_R$  with

(a) an alkoxy compound; and

(b) a diluent gas comprising a  $C_2$ - recycle gas, a  $C_{3+}$  recycle gas, steam, hydrogen, or mixtures thereof,

to form a combined gas stream wherein in the combined gas stream;

1. the alkoxy compound is present in a quantity that provides an alkoxy equivalent which exceeds that added to the preceding MTG reaction zone from which the effluent product gas was formed; and

2. the diluent gas composition is of a temperature and composition and is present in an amount that:

(a) provides for the combined gas stream to have a temperature of from about 650°F to about 720°F, and

(b) provides for the combined gas stream to have specific heat content that limits temperature increase of the gas stream to less than 150°F upon reaction of the alkoxy compound content thereof to hydrocarbon compounds;

(c) provides for a total water content following reaction of the alkoxy compound to hydrocarbon compounds that does not exceed a partial pressure of water (as steam) of 2.2 ata; and

contacting the combined gas stream with an MTG catalyst in a succeeding reaction zone to form a new effluent product gas.

-52-

1           2.    The method of claim 1, wherein the combined gas  
2   stream has a temperature of from about 700 to about 720°F,  
3   and the temperature increase of the gas stream is less than  
4   100°F.

1           3.    The method of claim 2, wherein the alkoxy  
2   compound is DME and the diluent gas comprises a  
3   C<sub>2</sub>- recycle gas and a C<sub>3+</sub> recycle gas in a molar ratio of C<sub>2</sub>-  
4   :C<sub>3+</sub> of from about 3:1 to about 1:3,

1           4.    The method of claim 3, wherein the diluent gas  
2   contains from about 10 to about 50 mole % of hydrogen.

1           5.    The method of claim 1, wherein from three to ten  
2   MTG reaction zones are arranged in series flow and the  
3   combined gas stream comprising the effluent gas product  
4   from a preceding MTG reaction zone and the alkoxy compound  
5   and diluent gas is at a temperature of from about 675 to  
6   about 720°F when first contacted with an MTG catalyst in a  
7   succeeding MTG reaction zone and has a specific heat  
8   content that provides for a temperature of effluent gas  
9   exiting the succeeding zone of from about 730 to about  
10   800°F.

1           6.    The method of claim 5, wherein with respect to  
2   each MTG reaction zone each combined gas stream enters each  
3   zone at substantially the same inlet temperature and each  
4   effluent gas exits each zone at substantially the same  
5   outlet temperature.

1           7.    The process of claim 6, wherein the partial  
2   pressure of water in an effluent gas does not exceed 2.2  
3   ata.

1           8.    The method of claim 1, wherein the alkoxy  
2   compound and diluent gas are preheated to a temperature of

-53-

3 from about 450 to about 550°F prior to being combined with  
4 the effluent gas product from a preceding MTG reaction  
5 zone.

1 9. The method of claim 8, wherein the combined gas  
2 stream has a temperature of from about 650 to 720°F and the  
3 temperature increase of the gas stream is about 85°F or  
4 less.

1 10. The method of claim 9, wherein the alkoxy  
2 compound is DME and the diluent gas comprises a C<sub>2</sub>- recycle  
3 gas and a C<sub>3+</sub> recycle gas in a molar ratio of C<sub>2</sub>:C<sub>3+</sub> of from  
4 about 3:1 to about 1:3.

1 11. The method of claim 1, wherein a series of MTG  
2 reactors is employed and the combined gas stream supplied  
3 to the last MTG reactor of the series has a temperature of  
4 from about 650 to 700°F and a specific heat content that  
5 limits the new effluent product gas temperature to 760°F or  
6 less.

1 12. The method of claim 11, wherein the combined gas  
2 stream supplied to the MTG reactors other than the last MTG  
3 reactor of the series has a temperature of 710 to 730°F and  
4 a specific heat content that limits its temperature  
5 increase to a range of 70 to 90°F.

1 13. The method of claim 1, wherein a series of MTG  
2 reactors is employed and a portion of the effluent product  
3 gas from the first MTG reactor is recycled back to the  
4 first MTG reactor inlet to become admixed with feedgas to  
5 the first MTG reactor to form a combined gas stream feed to  
6 the first MTG reactor having a temperature of from about  
7 650 to 720°F and a specific heat content that limits  
8 temperature increase of the gas stream to less than 150°F.

-54-

1           14. The method of claim 13, wherein the combined gas  
2 stream feed to the first MTG reactor has a temperature of  
3 from about 650 to about 720°F and a specific heat content  
4 that limits temperature increase of the gas stream to 100°F  
5 or less.

1           15. The method of claim 1, wherein the diluent gas  
2 contains steam in an amount sufficient to provide for a  
3 partial pressure of steam in the new effluent product gas  
4 of from about 1.95 to about 2.2 ata.

1           16. The method of claim 1, wherein a series of MTG  
2 reactors is employed, and of that total quantity of alkoxy  
3 compound converted to hydrocarbon compounds, no more than  
4 20% of the total alkoxy compound is converted in the first  
5 MTG reactor of the series.

1           17. The method of claim 1, wherein each effluent gas  
2 product has a partial pressure of water of from 1.85 to 2.2  
3 ata.

1 / 2

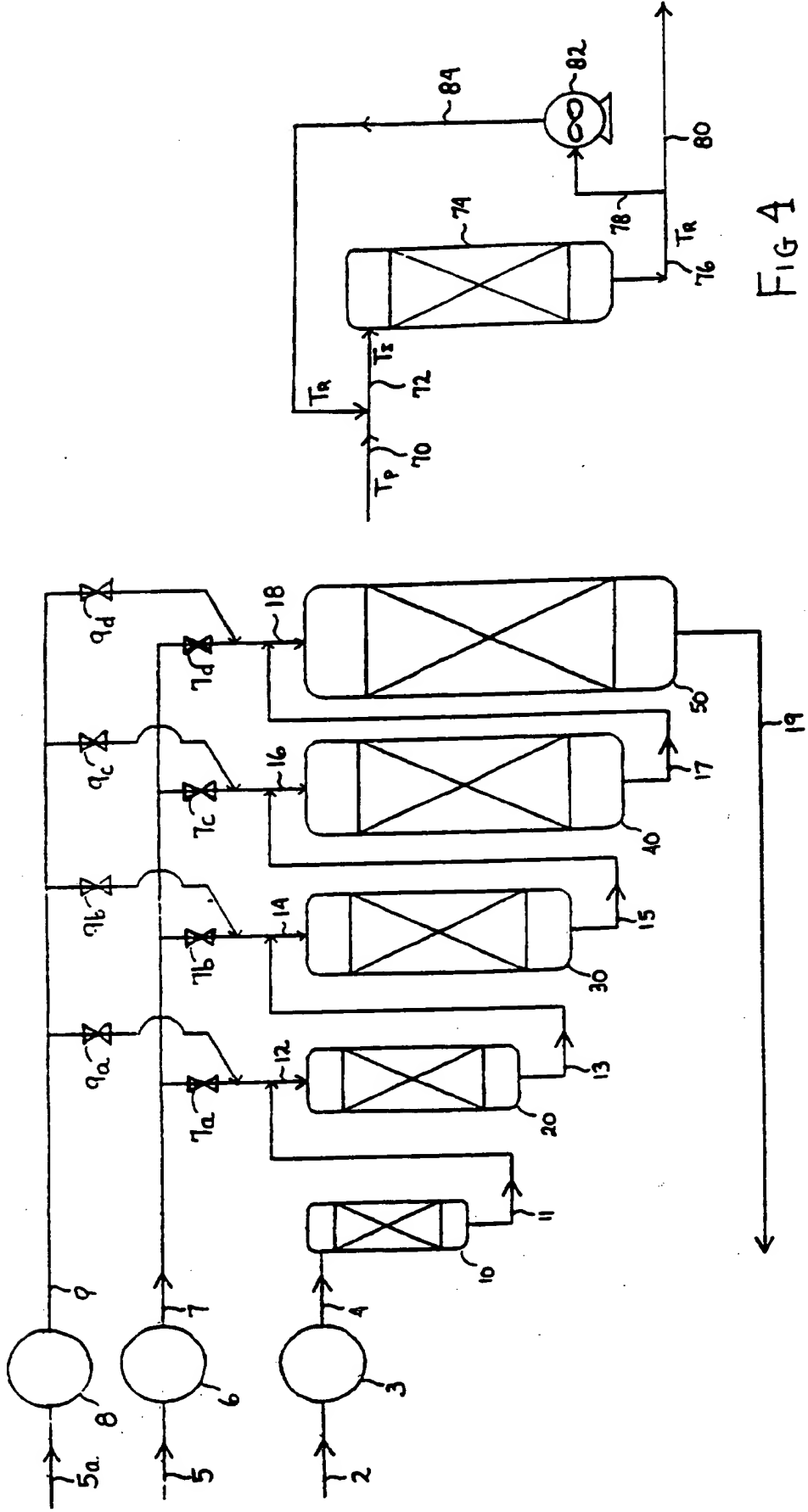


Fig 1

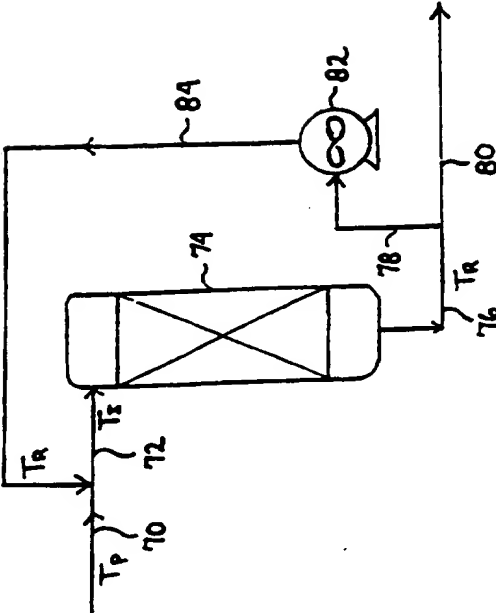


Fig 4

2 / 2

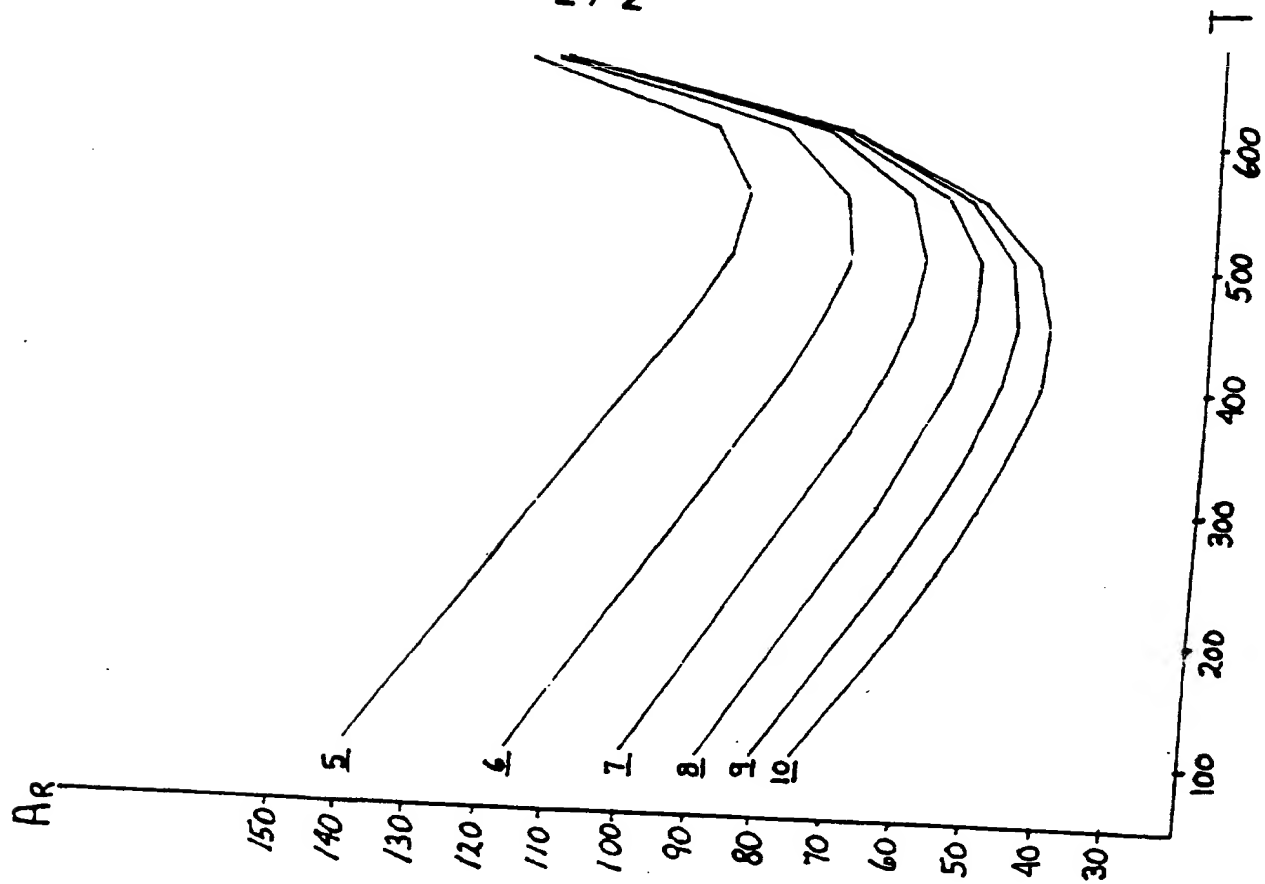


Fig. 3

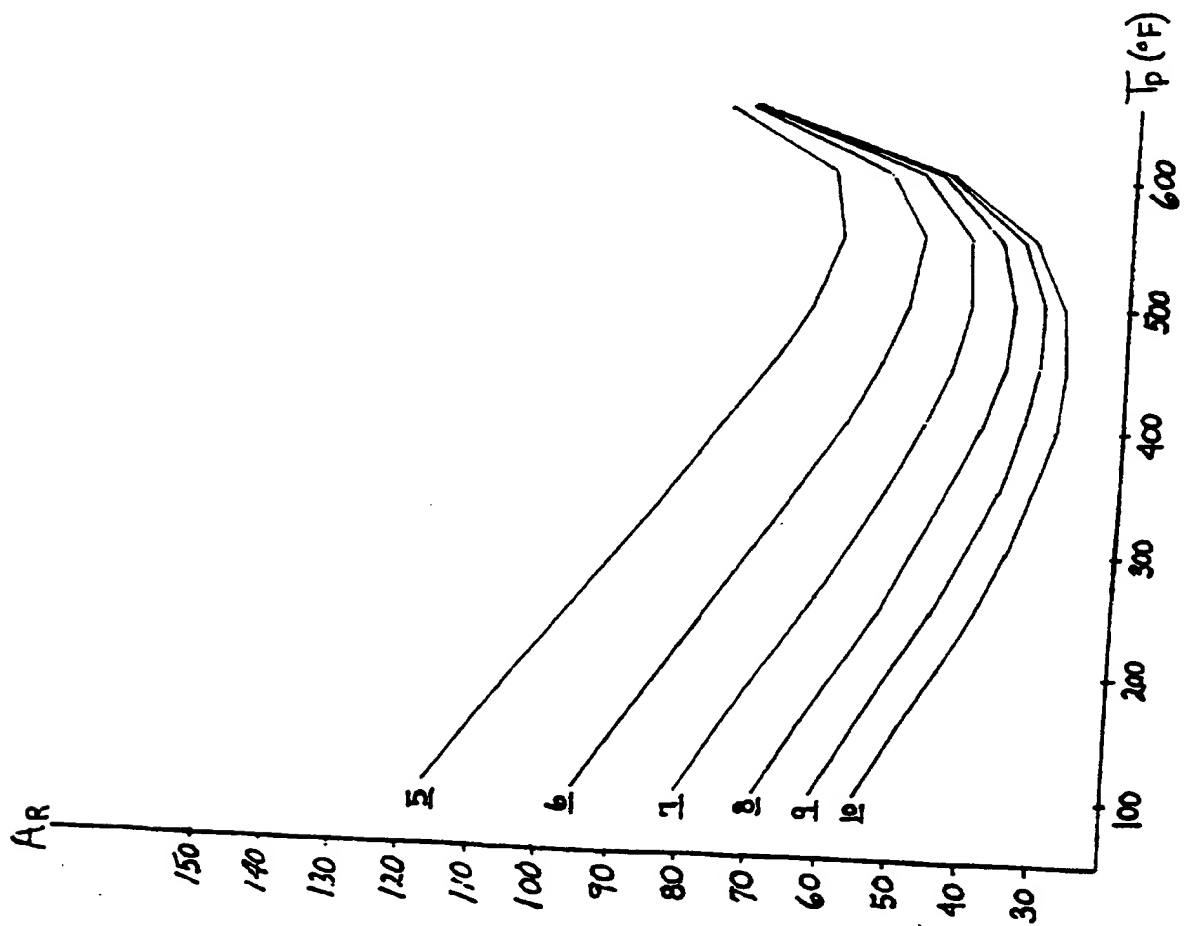


Fig. 2

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/14397**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C07C 1/20, 1/22

US CL : 585/408, 469, 639

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/408, 469, 639, 315, 733

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Extra Sheet.**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,035,430 (DWYER ET AL) 12 July 1977, col. 8 lines 66-69; col. 9, lines 1-9; col. 9 lines 13-20	1-4, 11-17
Y	US, A, 4,404,414 (PENICK ET AL) 13 September 1983, col. 6., lines 36-58; col. 9, lines 39-53, especially, line 47.	1-4, 11-17
A	US, A, 4,547,602 (TABAK) 15 October 1985	
A	US, A, 3,931,349 (KUO) 06 JANUARY 1976	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		
* E	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* L	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* O		
* P	* A	document member of the same patent family

Date of the actual completion of the international search

26 FEBRUARY 1996

Date of mailing of the international search report

20 MAR 1996

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

GLENN CALDAROLA

Telephone No. (703) 305-6118

Form PCT/ISA/210 (second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/14397

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS ,

search terms: (serial,plural,sequen?,casade?);(reactor?,cataly?,stage?);(585\*408,469,639,733,315/ccls)





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification<sup>6</sup> :

C07C 1/20, 1/22

A1

(11) International Publication Number:

WO 96/15082

(43) International Publication Date:

23 May 1996 (23.05.96)

(21) International Application Number: PCT/US95/14397

(22) International Filing Date: 7 November 1995 (07.11.95)

(30) Priority Data:

08/336,430

9 November 1994 (09.11.94)

US

(71) Applicant: STARCHEM, INC. [US/US]; 10822 Fawnview Drive, Houston, TX 77070 (US).

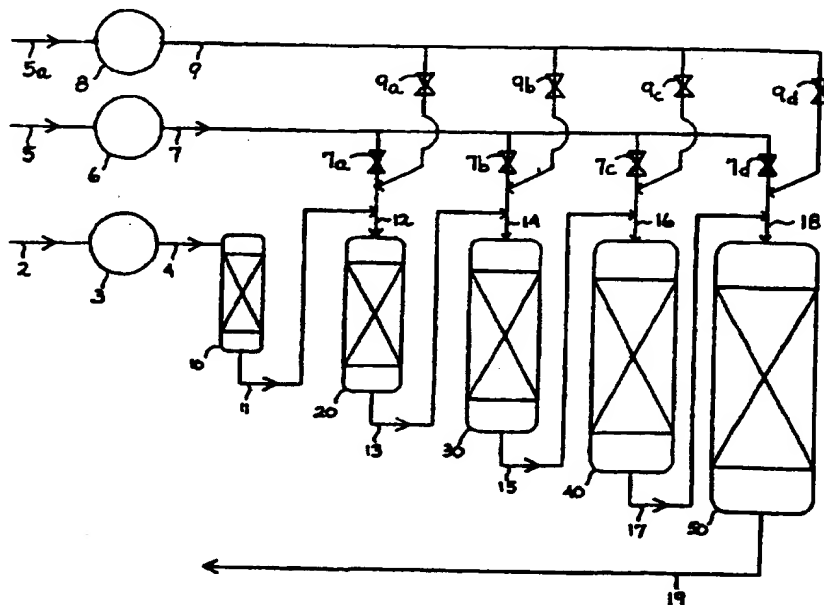
(72) Inventor: VAN DIJK, Christiaan, P.; 10722 Glenway, Houston, TX 77070 (US).

(74) Agents: COX, Charles, M. et al.; Pravel, Hewitt, Kimball &amp; Krieger, P.C., 10th floor, 1177 West Loop South, Houston, TX 77027-9095 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).

**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: CONVERSION OF METHANOL TO GASOLINE

**(57) Abstract**

This invention relates to a process for converting alkoxy compounds into hydrocarbon compounds, mostly in the gasoline boiling range. This invention provides energy savings in the conversion of alkoxy compounds compared to conventional catalytic MTG serial fixed bed operations. In this process, fresh alkoxy feedstock (5) is fed to each reaction zone combined with an effluent gas product from a preceeding MTG reaction zone (11, 13, 15, 17) together with additional diluent gas (5a). An alkoxy equivalent is provided to each reaction zone in an amount which exceeds that added to a preceeding MTG reaction zone from which the effluent product gas was formed. The diluent gas temperature and composition is such that it maintains temperature increases in each successive zone to less than 150 degrees F. and water partial pressures less than 2.2 ata.

\* (Referred to in PCT Gazette No.36/1996, Section II)

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

TITLE: CONVERSION OF METHANOL TO GASOLINE

SPECIFICATION

FIELD OF THE INVENTION

5 This invention relates to a process for converting alkoxy compounds into hydrocarbon compounds, mostly in the gasoline boiling range.

BACKGROUND OF THE INVENTION

Catalysts for the conversion of alkoxy compounds, such as methanol and/or dimethyl ether, to gasoline grade hydrocarbon products have been known since the 1970's.  
10 Processes for the conversion of natural gas and/or coal to methanol have been known for a much longer period.

Since the advent of a catalyst for the conversion of methanol to gasoline as disclosed by various Mobil Oil Corporation patents issued beginning in the 1970's,  
15 worldwide only one commercial installation which practices the methanol to gasoline ("MTG") process with a Mobil-type MTG catalyst has come into being. That installation is in New Zealand.

Conceived in the late 1970's when crude oil prices  
20 were in the \$30-\$40/barrel range -- with projections for even further price increases -- the New Zealand installation then appeared to be economically feasible. As then envisioned, and as now existing, the New Zealand facility is basically a natural gas to methanol plant (as  
25 the front end) coupled to a methanol to gasoline plant operating with an MTG catalyst in a plurality of fixed catalytic bed reactors arranged in parallel, each for single pass gas flow. The arrangement comprises five MTG reaction vessels, four of which operate at any given time  
30 and one is off stream for MTG catalyst regeneration or replacement.

Between the conception of the New Zealand facility with its attendant capital and operational cost commitments

-2-

and the time that the facility was completed and ready for on-stream operations (at a capital cost obligation of about \$1.2 billion) the worldwide price of crude oil drastically declined to its current day levels of about \$20/barrel. At today's cost of crude oil, gasoline produced from methanol by a process as followed in the New Zealand facility is competitively uneconomical in comparison to gasoline refined from crude oil. In the first place the New Zealand approach is too costly in the conversion of natural gas into methanol. The present inventor, together with Lowell D. Fraley, has described a natural gas to methanol conversion process with much lower expected capital costs in U.S. Patent Nos. 5,177,114 and 5,245,110. Yet, even with this expected lower cost for methanol the New Zealand process of converting methanol to gasoline is still too high in capital cost. A major reason that the methanol to gasoline part of the New Zealand facility is uneconomical is because of the heat exchange duties -- both in capital and operational cost -- required for proper operation of a Mobil-type methanol to gasoline catalyst (MTG catalyst). For proper operation of an MTG catalyst in terms of its activity and aging, it must be exposed to a particularly controlled environment of temperature and water concentration while it is in contact with the methanol (or other oxygenated compounds) that it converts to gasoline grade hydrocarbons. If exposed to too low of a temperature, an MTG catalyst will not be active or will be of such low catalytic activity to be of no interest. Exposed to too high of a temperature, the MTG catalyst will so prematurely "age" and/or be destroyed so as to be economically impractical for use.

This problem of the temperature sensitivity of an MTG catalyst is compounded by the problem of its need for the presence of water in order for it to be catalytically active. Too little water in its presence and it is inactive or of such low activity to be of little practical interest. Depending upon its temperature exposure, too

-3-

high a concentration of water and the MTG catalyst ages so prematurely and/or is destroyed so as to render its economical use unfeasible.

5        These temperature/water sensitivity problems attendant to use a MTG catalyst are further complicated by the fact that the reaction of methanol (or other oxygenated compounds) to gasoline which it catalyzes is fast and highly exothermic, thus causing a high degree of heat release (i.e., heat of reaction) at the site of the desired  
10       reaction. If not moderated by some means, a methanol and/or dimethyl ether feedstock fed into contact with an MTG catalyst at 710°F would react in contact with the catalyst to form a product gas having a temperature greater than 2,000°F. Such a temperature rise within an MTG  
15       reaction vessel is not acceptable. Nor can the heat released by the MTG reaction be controlled within acceptable product gas exit temperature limits -- i.e., 730°F to 800°F -- by direct heat exchange methods, because the reaction MTG is too fast.

20       The need of an MTG catalyst for a sufficient, though limited, exposure to water coupled with its need for exposure to a sufficient, though limited, range of temperature to be sufficiently active, coupled to the fact that it catalyzes a fast and highly exothermic reaction,  
25       have entailed a number of processing complexities associated to the heat exchange requirements attendant to the proper operation of a methanol to gasoline process with an MTG catalyst.

30       In order to accommodate the temperature range exposure requirements of the MTG catalyst, the New Zealand facility effectuates product gas temperature control within the MTG catalyst vessels by recycle of the C<sub>2</sub>- and C<sub>3</sub>-hydrocarbon by-product gases remaining after the reactor product gases are cooled down from their reaction temperature of about 800°F  
35       to about 100°F for removal of their gasoline grade hydrocarbon product content. In order to limit the temperature rise in the MTG reaction to less than about

-4-

100°F, this recycle diluent gas is added in an amount compared to the methoxy feed gas (methanol, dimethyl ether, etc.) of about 12.4 moles diluent recycle/mole methoxy equivalent. For every 1 volume of methoxy equivalent with which it is combined to form the feedstock gas it is therefor necessary to heat about 12.4 volumes of the C<sub>2</sub> and/or C<sub>3+</sub> recycled diluent gas from its recovery temperature of about 100°F to the minimum temperature required by an MTG catalyst for sufficient activity, which is about 650°F and preferably about 700°F. This imposes a tremendous heat exchange burden both in terms of reactor effluent gas cool down (800°F to 100°F) for gasoline product recovery and recycle gas (C<sub>2</sub>-/C<sub>3+</sub>) reheat (from 100°F to at least 650°F, and preferably to 700°F). For each volume of hydrocarbon product produced and recovered about 71 volumes of recycle diluent gas must be heated up by about 600°F and later cooled down by about 700°F in adiabatic heat exchanger units by heat exchange first with a new portion of cool feed gas and then by cooling water or a refrigerant.

In the New Zealand operation the methoxy compound, generally in the form of an equilibrium mixture of methanol, dimethyl ether and water vapor, is combined with a recycle gas comprising C<sub>2</sub>-and C<sub>3+</sub> hydrocarbons and the methoxy content is reacted in a single pass over an MTG catalyst to produce a product gas of about 800°F with a partial pressure of water (as steam) of about 2 atmospheres absolute (ata) at a product gas pressure of about 22.3 ata. Hence, heat exchange operations to heat up feed gases and/or cool down product gas are carried out on gas streams at a pressure of about 22.3 ata.

The MTG reaction gases are cooled from their reaction temperature, T<sub>R</sub>, to their final cooldown temperature, T<sub>0</sub>, in two heat exchange operations. In the first operation the reaction gases are indirectly heat exchanged with feed gases through adiabatic heat exchangers to cause the feed gases to warm up from their unit available temperature of

-5-

about  $T_0$  to their reactor inlet temperature  $T_I$  by transferring thereto of a quantity of heat  $Q$  from the reaction gases which thus causes the reaction gases to cool down from their reaction temperature  $T_R$  to their first  
5      cooldown temperature  $T_X$ . Thereafter, the reaction gases are finally cooled from their first cooldown temperature  $T_X$  to the liquid hydrocarbon recovery temperature,  $T_0$ , either by direct or indirect heat exchange contact with chill water.

10           For purposes of discussing the heat exchange burden associated to operation of the New Zealand process, one may assume that the specific heat content of a feed gas about equals the specific heat content of the reaction product gas which results therefrom. Under this circumstance, when  
15      the reaction product gas gives up a quantity of heat  $Q$  to heat up a new portion of feed gas from  $T_0$  to  $T_I$  the reaction gas cools to a temperature  $T_X = T_R - (T_I - T_0)$ . To finally cool the reaction gas to a temperature  $T_0$  to recover its liquid hydrocarbon content the quantity of heat  
20      that must be removed from the reaction product gas is that additional quantity of heat resulting from the heat of reaction of the alkoxy compound from which the reaction gas was formed.

25           Generally, the adiabatic heat exchangers through which feed gas is heated up while reaction product gas is cooled down are on the order of 3-4 times as expensive as those heat exchange units by which the product gas is finally cooled down by heat exchange with chill water. Further, the sizing of each of these heat exchange units, which  
30      bears very significantly on their cost, is directly effected by the difference in temperature to which the feed gases are to be heated and the temperature from which the product gas is to be cooled ( $\Delta T$ ) and the pressure ( $P$ ) of the gases to be heated and cooled. The larger the  
35      differential temperature ( $\Delta T$ ) and/or the higher the pressure the more efficient the heat exchange process and the smaller can be the size of the heat exchanger needed.

-6-

The relative heat exchange surface area ( $A_R$ ) required to transfer this quantity of heat ( $Q$ ) is generally given by the formula  $A_R = Q (1/\Delta T) (1/P)^{0.6}$ .

5        Suggestions have appeared in the prior art which are directed to ameliorating this tremendous heat exchange burden. Mobil Oil Corporation's U.S. Patent 4,035,430 to Dwyer et al. describes an MTG process wherein a number of spaced apart MTG catalyst beds are employed and hydrocarbon recycle gas may be injected between the successive beds to  
10        control the exotherm. Also described is the possibility of interbed injection of methanol or DME as a quench to maintain the temperature rise in each MTG catalyst bed to about 50°F with a total temperature rise over all beds to about 200°F. This however, as Mobil's later U.S. Patent  
15        4,404,414 to Penick et al. notes, requires either that the conversion of the alkoxy feed in each MTG reactor be limited to a relatively low value (which is difficult to control at the high reaction rate in contact with the catalyst) or, alternatively, that an extraordinarily high  
20        recycle ratio must be used, neither being an attractive possibility.

      Mobil's U.S. Patent No. 4,404,414 to Penick et al. provides yet another suggestion. It describes the use of the reactor effluent gas of a preceding MTG reactor, for  
25        admixture with a fresh charge of alkoxy compound (DME and/or methanol) to be fed to a succeeding MTG reactor, as the medium for heating up the new alkoxy charge of combined gas mixture to the inlet temperature desired for reaction in a succeeding MTG reactor. According to Penick et al.'s  
30        suggestion the total quantity of temperature-control diluent gases used in the process is passed through the first MTG reactor and hence into the succeeding MTG reactor without the need for cooldown heat exchange of the diluent gas from the reaction gas temperature (about 800°F) to  
35        about 100°F for purposes of product recovery and thereafter reheat from about 100°F to an inlet reaction temperature (about 700°F) for recycle use with the new alkoxy charge.



-7-

This reduces the overall effective volume of recycle gas as a ratio to the final product make required for proper temperature moderation in the MTG reactors. However, this heat exchange savings is purchased at the risk of advanced aging of the MTG catalyst in the succeeding MTG reactor that may result from the successive accumulation of water (steam) content that results from the buildup of water as a by-product of the MTG reaction that occurs within both the preceding and succeeding reactors. For example, for each mole of hydrocarbon produced, the hydrocarbon product from crude methanol having a water content of about 6 wt.% or from an equilibrium methanol-dimethyl ether mixture produced therefrom contains about 6.45 moles of water. Addition of a diluent gas to this methoxy compound in an amount sufficient to moderate the temperature rise in a first MTG reactor as desired, followed by addition to the first reactor product gas of an equivalent amount of new methoxy compound to form a feed gas stream for reaction in a second MTG reactor results in a product gas from the second reactor having nearly double a mole fraction of water as that of the product gas from the first MTG reactor.

Accordingly, in the process proposed by Penick et al. where both reactors are operated at about the same pressure the concentration of water (as steam) to which the MTG catalyst of the succeeding MTG reactors is subjected is substantially greater than that to which the MTG catalyst of the preceding MTG reactor is exposed. This, as Penick et al. notes, inevitably leads to the dilemma that if both reactors are operated at about the same temperature either the MTG catalyst in a preceding MTG reactor must be underutilized by depriving it of exposure to a water content that optimizes its potential for activity or the MTG catalyst in a succeeding MTG reactor must be overexposed to water such that it ages prematurely. This dilemma of Penick et al.'s proposal necessitates a significant difference in the operational conditions of temperature or

-8-

pressure between the preceding and succeeding MTG reactors, which, in order to maximize both the activity and operational life of the MTG catalyst in each, results in an undesirable change in hydrocarbon product's compositional distribution produced in each.

Yet another Mobil Oil Corporation U.S. Patent No. 4,788,369 to Marsh et al. suggests a method for improving the economies of even the Penick et al. process that involves the separation of the  $C_{3+}$  by-product hydrocarbon gases from the  $C_2$ -by-product hydrocarbon gases and thereafter use of the  $C_{3+}$  hydrocarbon gases as the recycle diluent gas required for temperature moderation. Because of the higher specific heat of the  $C_{3+}$  recycle, following the suggestion of Marsh et al. the volume of recycle diluent gas required for practice of the MTG process may be reduced. As Marsh et al. notes, in terms of compressor duties a  $C_{3+}$  recycle gas is more readily and economically processable for recycle use than is a  $C_2$ - recycle gas. However, a smaller amount of the  $C_{3+}$  recycle gas volume necessitates use of a lower total pressure for processing if the steam vapor pressure is to be kept the same as before. That lower pressure has a negative effect on the heat exchange capability of the process. Thus, the only advantage remaining for the Marsh approach is the use of fewer moles of recycle gas which thus reduces compressor duties. The disadvantages of increased heat exchange surface requirements resulting from the lower pressure of operation reduces, and might even outweigh, the savings in the recycle compressor. It suffices to say that the Marsh et al. patent does not succeed in diminishing the heat exchange requirements of the process. Yet, even with use of a  $C_{3+}$  hydrocarbon by-product gas as a recycle to save on compressor duties as suggested by Marsh et al. the savings in capital and operational cost of the Marsh et al. process requirements are modest, at best.

The temperature rise/water concentration dilemma that hamstrings the MTG conversion process over an MTG catalyst

-9-

as being an economically competitive process for gasoline production compared to that of gasoline refined from natural crude oil remains unsolved by any prior art suggestion. Given the abundance of natural gas reserves from which the production of gasoline grade products is technologically possible, a solution to the economical obstacle to its conversion to gasoline is a greatly desired goal.

#### SUMMARY OF THE INVENTION

In accordance with the process described by this invention, it is possible to substantially reduce the heat exchange duties entailed in the proper operation for activity and aging regulation of an MTG catalyst while also properly controlling the exposure of such catalyst to a water concentration.

To significantly reduce the heat exchange requirements for proper temperature control of the reaction of an alkoxy compound over an MTG catalyst, and at the same time control the steam partial pressure in the process within narrow limits, aiming thus to have the reaction proceed under proper temperature and steam pressure control without at any time endangering the MTG catalyst, the invention proposes a method for operation of an MTG process wherein:

(1) Successive reaction zones containing an MTG catalyst are employed wherein a product effluent gas of temperature  $T_{r_p}$  from a preceding MTG reaction ( $r_p$ ) is combined with a new charge of feed gas comprising an alkoxy compound and a diluent gas comprising a  $C_2$ -recycle gas, a  $C_3$  recycle gas, steam, hydrogen, or mixtures thereof, which new charge of feed gas has been preheated to a temperature  $T_p$  that is less than  $T_{r_p}$ , and the mixture of the new charge of feed gas with the product effluent gas forms a combined gas mixture that is of a desired temperature  $T_1$  and specific heat content to be contacted with an MTG catalyst in a succeeding reaction zone ( $r_s$ ) to convert its alkoxy compound content to hydrocarbon products contained in a new product gas stream having a temperature

-10-

Tr<sub>s</sub>. In warming up the new alkoxy-recycle feed gas charge from the preheat temperature T<sub>p</sub> by mixing with the earlier hot effluent gas to obtain a combined gas mixture of temperature T<sub>i</sub>, the warmup is obtained without heat exchangers, which otherwise would have been necessary to warm the new feed gas up to the desired reactor inlet temperature; further the lower diluent recycle content of the fresh feed gas would not allow entry of that feed as such at the desired reactor inlet temperature without its reaction to a temperature greater than the Tr<sub>s</sub> temperature desired for the outlet from the reactor.

(2) The new charge of alkoxy compound provides an alkoxy equivalent value which exceeds that which was added to the preceding MTG reaction zone and the new charge of diluent gas provides the combined gas stream with a specific heat content that upon reaction of the new charge of alkoxy compound to hydrocarbon compounds limits the temperature rise ( $\Delta T_R$ ) within the succeeding reaction zone to less than 100°F and preferably less than 75°F.

(3) The new charge of alkoxy compound and diluent gas are preheated before combination with the product effluent gas to a temperature T<sub>p</sub> that is below the desired reactor inlet temperature T<sub>i</sub>, so that on taking an appropriate amount of this new charge for addition to the effluent gas from the preceding reactor a mix temperature of T<sub>i</sub> will be obtained, whereafter contacting the combined gas mixture with a sufficient amount of MTG catalyst the succeeding reaction will produce a new effluent gas temperature of T<sub>R</sub>, which is at a desired level. As desired, each MTG reactor in the series may be operated with the same T<sub>i</sub> and T<sub>R</sub> temperatures or any reactor within the series may be operated at a T<sub>i</sub> and T<sub>R</sub> temperature selected for it which is different than that of other reactors in the series, this being accomplished by the proper choice of the alkoxy and recycle content of the new feed gas charge to be added to the succeeding reactor and the quantity of this new feed

-11-

charge to be combined with the product effluent gas from the preceding reaction.

(4) As desired, a portion of the new charge of diluent gas may comprise water in an amount that together with the water carried over with the product effluent gas and the water formed by reaction of the new charge of alkoxy compound provides a total water content in the new product effluent gas that at the outlet pressure of the succeeding MTG reaction zone provides for any partial pressure of water desired, which preferably will not exceed 2.2 ata, and preferably will be in the zone of 1.85 to 2.2 ata, most preferably in the zone between 1.95 and 2.15 ata.

In its general form the process of this invention may seem complicated with respect to how the process conditions can be set and kept at necessary conditions in order to achieve the desired goal. Therefore the invention will first be explained in its simplest form. Assume that it is desired to have a series of reactors, in all of which the reaction of the methoxy compounds is taking place in the same reaction temperature zone ( $T_I$  to  $T_R$ ) and also where all the reaction product gases have identical steam vapor pressures.

This target can be achieved even though substantial pressure drops exist between reactor zones. Again, it is easier to explain the invention if the simplifying assumption is made that the pressure drop between reactors is so small that it can be ignored.

It is clear that given a chosen composition of the diluent recycle, conversion of a given amount of a given methoxy compound can be kept in a single reactor in a desired reaction temperature zone, say from 700 to 800°F, by proper choice of the quantity of the diluent recycle gas added to the methoxy compound. Choose now, however, a smaller quantity recycle gas, which would then necessitate a larger reaction temperature zone, but with the same final temperature, say between 600 and 800°F. Also choose a pressure at which to operate so that on reaction the

-12-

resulting water vapor partial pressure is at the desired level.

Now take a large quantity of such an alkoxy-recycle gas mixture and preheat that to the temperature of 600°F, but do not as yet contact the so preheated gas with the MTG catalyst. Take a starter gas stream at the desired final temperature level of 800°F with the desired level of water vapor partial pressure at the desired total pressure. Such a starter gas stream could be of any composition, but could conveniently be made from the same alkoxy compound in admixture with a similar diluent recycle composition, but in a larger recycle amount, so that that the starter stream could be warmed up to 700°F and contacted with MTG catalyst to react to a product gas having a temperature of 800°F.

Now take of the new mixture of alkoxy and recycle that has been preheated to 600°F, and in a sufficient amount mix it with the hot starter gas stream which is at 800°F to arrive at a combined gas stream having a temperature of 700°F. On reaction of the alkoxy content of the combined gas stream over an MTG catalyst the final temperature of the product gas will then be 800°F, because each component part of the combined gas stream was once at or could react to this temperature.

The product gas stream at 800°F, thus obtained, serves in its own turn as a hot gas source for admixture with a new portion of the 600°F gas mixture containing new alkoxy compound to arrive at a still larger volume 700°F combined gas stream which again can be contacted with an MTG catalyst to form a product gas stream at 800°F. This alternating mixing and reaction is continued until all the alkoxy containing gas mixture of 600°F has been reacted.

When pressure drop across the MTG reactor(s) is sufficiently large to have to be taken into account; then on each addition of the 600°F alkoxy-containing gas a sufficient amount of steam may be added also, so as to arrive at the desired water partial pressure at the resulting lower total pressure due to pressure drop. A

-13-

reduction is then needed of the amount of the diluent recycle gas content of the new charge by an amount that corresponds to the specific heat content of the added steam, so that the (slightly) changed 600°F stream still  
5 will be able to react to 800°F. Alternatively, with no alteration of the alkoxy-containing gas mixture, the same results can be obtained by adding the requisite amount of 800°F steam to the product effluent gas or to the 600°F alkoxy-containing gas.

10 The given procedure can obviously also be applied to a narrower reaction temperature zone than 700 to 800°F and to different starting temperatures for the gas mixture subjected to reaction than the value of 600°F chosen for this discussion.

15 It is also clear that it is possible to vary the steam partial pressure from reactor to reactor, if desired. Such steam partial pressure variations are easier in an upward direction than downward.

20 A further advantage is that the temperature zone of reaction can be varied at will from reactor to reactor by changing the amount added of the new alkoxy-recycle charge and its preheat temperature.

25 It should therefore be clear, that this invention provides a feasible method to have the MTG reaction proceed within desired limits of temperature and also attain the desired water vapor partial pressure levels in the exit of each of the reactors.

30 It is the primary intent of this invention to lower the cost of the heat exchange which is a major cost item in the New Zealand design. However, it should also be pointed out that the present invention opens the possibility for operating a series of reactors under an innovative temperature and steam partial pressure approach.

35 It has been discussed in the literature that at low temperature a large percentage of aromatic hydrocarbons are formed in the MTG reaction. When the MTG reaction then proceeds to higher temperatures, the aromatics previously

-14-

formed are alkylated with the methanol which is still being reacted at these higher temperatures. When it is desired to lower the content of higher alkylated aromatics, like durene and even the trimethylated benzenes (as presently  
5 desired for achieving a high quality reformulated gasoline), with this invention it then becomes feasible to operate the first set of MTG reactors at a higher inlet temperature, thus lowering the formation of aromatics to a very low amount and only in the last MTG reactor allowing  
10 operation at a lower temperature, but finishing the reaction in that lower temperature zone. This thus translates to an operation of the first four of, say five, reactors at a temperature zone of for instance 720 to 790°F, while the last MTG reactor can be kept within the  
15 narrow temperature limits of for instance 700 to 740°F. The larger amount of aromatics formed in the last reactor can then not be further alkylated above the 740°F temperature.

According to this invention the total amount of alkoxy  
20 equivalent processed to hydrocarbon products is proportioned among a plurality of MTG reaction zones and the alkoxy equivalent quantity provided to each MTG reaction zone generally increases in progression from the first to the last or final MTG reaction zone. This method  
25 of operation provides for great flexibility in the operational conditions of temperature and pressure at which a given MTG reaction zone may be operated relative to another in order to achieve a variety of desirable objectives, all attendant with a significant reduction in  
30 the heat exchange duties otherwise required to process the same total amount of methoxy equivalent to hydrocarbon products by prior MTG processing methods.

For instance, where the activity of the MTG catalyst is the same in each zone, for uniformity of product  
35 distribution of hydrocarbon product produced in each MTG reaction zone, each desirably is operated at approximately the same pressure, the same inlet and outlet temperatures



-15-

(i.e., each zone has the same  $\Delta T_R$ ), and each reaction zone, at least after the first, has about the same partial pressure  $H_2O$  at the outlet of the reaction zone. Such is possible with the method of the invention. However, if  
5 because of aging or other reasons the activity of an MTG catalyst in one of the multiple zones is significantly less than another, it may be desired to operate this particular MTG reaction zone at a higher outlet partial pressure of  $H_2O$  than the other, or at a higher  $T_R$ , this in order to  
10 enhance the activity of the MTG catalyst therein. This too is possible with this invention.

A combination of factors leads to a significant reduction in the heat exchange duties required by the process of this invention in comparison to prior MTG  
15 processes employed or proposed. First, on the bases of the total methoxy equivalent ("MeO eq.") processed, with the process of this invention the diluent gas/MeO eq. mole ratio is reduced which in turn reduces the quantity of diluent gas that through adiabatic heat exchange units must  
20 be preheated for reaction temperature moderation use or, ultimately, cooled down for recovery of hydrocarbon product. This reduces the size of the heat exchangers required for feedstream heatup and/or final product cooldown. Further, a significant quantity of the total  
25 methoxy equivalent processed, together with the recycle diluent gas needed to moderate its heat of reaction, needs to be preheated to a temperature ( $T_P$ ) which is lower than the temperature ( $T_I$ ) at which it is desired to contact the methoxy compound with an MTG catalyst. This is achieved by  
30 admixing the methoxy-recycle feed with hot product gases from a preceding MTG reaction (at  $T_R$ ) which heats up the added methoxy-recycle feed to the desired reaction inlet temperature, while cooling down the hot reaction gases to the desired reaction inlet temperatures. In this respect  
35 this aspect of the feed gas heatup/product gas cool down is performed by direct gas-gas contact, thus eliminating this portion of need for adiabatic heat exchange equipment.

-16-

Also, with respect to the warmup of feedstock gases to  $T_p$  by heat exchange with reaction gases at  $T_R$  through an adiabatic heat exchanger, this also increases the heat exchanger differential temperature ( $\Delta T$ ) making the heat exchange process more efficient, meaning the heat exchanger need will be smaller.

As explained hereafter in greater detail, operations in accordance with this invention permit a selection of conditions in terms of (a) the nature of the methoxy feed, (b) the nature of the diluent gas composition, and (c) the temperature to which the feed gases are preheated before being mixed with reaction gases from a preceding MTG reaction; such that the MTG conversion can be achieved with the maximum of economy in terms of the capital and/or operational cost associated therewith.

#### DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a five reactor series with interstage feed of feed charges of alkoxy-recycle feedstock gases between the reactors in accordance with the present invention.

Figures 2 and 3 plot the effect on the required relative heat exchanger surface area ( $A_r$ ) required for performing feed gas warmup by product gas cooldown heat exchange operations in adiabatic heat exchange units in accordance with the process of the invention for different preheat temperatures  $T_p$  as employed in a series of from five to ten MTG reactors, wherein a pressure drop of 0.35 ata occurs across each reactor. The relationships illustrated are based upon the general equation  $A_r = Q(1/\Delta T)(1/P)^{0.6}$  wherein  $Q$  is the quantity of heat involved in a heat exchange operation;  $\Delta T$  is the temperature difference between the gases involved in the exchange, namely  $T_R - T_p = \Delta T$ ; and  $P$  is the pressure of the gases being heat exchanged. The alkoxy feed for Figure 2A is dimethyl ether (DME) and for Fig. 3 is a DME containing equilibrium mixture formed from a crude methanol containing 16.4 wt.% water. For comparison treatment of the same

-17-

quantity of an equilibrium mixture formed from methanol-water in a single reactor requires a relative heat exchange surface area of about 325.4 relative units when operated at a pressure of 22.06 ata to provide for the same partial pressure of steam in the product gas as that provided by the process as illustrated in Figure 3.

Figure 4 is a schematic illustration of an alternative embodiment of the process wherein the first of a series of five MTG reactors recycles a portion of its product gas back to the inlet of this first MTG reactor to provide a gas-to-gas exchange of heat with fresh alkoxy feed to this reactor to achieve its final warmup from its  $T_p$  temperature to the  $T_i$  temperature desired for contact with the MTG catalyst therein.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The practice of this invention requires an alkoxy feedstock, generally a MeOH and/or DME feedstock, various reaction vessels containing an MTG catalyst composition and devices for controlling the rate of feed of DME and/or MeOH and  $H_2O$  (as steam),  $C_2$ - and  $C_3$ - gas by-product as diluent recycle gaseous feedstock admixture components of the total feedstocks to an MTG catalyst containing reaction vessel.

The MeOH may be formed from a coal or natural gas starting material by any of the methods well known to those skilled in art. Preferably when produced from natural gas the methanol is produced by methods as described in U.S. Patent Nos. 5,117,144 and 5,245,110. Prior to the MTG reaction, and preferably so, the MeOH may be subject to contact with a dehydration catalyst as is well known in the art to convert it to an equilibrium mixture of MeOH, DME and  $H_2O$  and this gaseous mixture of oxygenated organic components which is a preferred alkoxy feed component for an MTG catalyst contact for conversion to a hydrocarbon product with production of by-product water. Most preferred is the use of DME alone as the alkoxy feed component. DME can easily be isolated from the equilibrium mixture and the remaining methanol-water can be

-18-

concentrated as to its methanol content and recycled back to contact with the dehydration catalyst to make more DME containing equilibrium mixture.

5 The MeOH and/or DME components, however made, are, in the process of this invention, brought into contact with an MTG catalyst composition, as described in U.S. Patent Nos. 4,404,414; 4,788,369 to Penick and Marsh as earlier discussed and in other Mobil U.S. patents, to catalyze  
10 their conversion into a hydrocarbon product, a significant portion of which is within the gasoline boiling point range. As a rule of thumb, the carbon atoms supplied by the methoxy content of the DME/MeOH feed gas composition are converted to a hydrocarbon product averaging a carbon atom content of about 5.8 -- i.e.,  $C_{5.8}H_{13.6}$ . This  
15 hydrocarbon product is, of course, comprised of a mixture of hydrocarbons which vary in carbon atom numbers from one up. The  $C_{1-5}$  carbon atoms products of this reaction are normally gaseous compounds and are recovered and at least a portion thereof is recycled as a diluent gas to become a  
20 part of a fresh alkoxy feedstock to an MTG reactor, together with traces of higher hydrocarbons. Most of the  $C_{5+}$  carbon atom hydrocarbon products are recovered as a "gasoline" or fuel grade product. The  $C_2-/C_{3+}$  hydrocarbon gas by-products of the MTG reaction which are recovered may  
25 be separated into separate  $C_2$ - and  $C_{3+}$  streams, and either alone or in desired combinations thereof recycled to the MTG process for purposes of temperature control.

In order to minimize the heat exchange duty requirements while regulating the temperature, pressure and  
30 water concentration conditions for the proper activity and aging regulation of an MTG catalyst during the conversion of alkoxy compounds to hydrocarbon products, the process of this invention utilizes a plurality of MTG catalyst zones or reaction vessels in series flow whereby the product  
35 effluent gas from any preceding MTG zone or reactor is combined with a fresh charge of alkoxy compound together with a recycle diluent gas and/or water (stream) to form a

-19-

combined gas steam of a temperature and specific heat content suitable as an alkoxy-containing feed gas to a succeeding MTG zone or reactor wherein its alkoxy compound content is reacted in contact with an MTG catalyst to hydrocarbon compounds. Generally, the alkoxy equivalent of the alkoxy compound added to the product effluent gas of a preceding MTG reaction exceeds the alkoxy equivalent content of the feed gas stream to the preceding reactor from which the product effluent gas was produced.

Any number of MTG reaction zones or reactors may be utilized, though generally no further practical advantage is realized in excess of ten, and more preferably five to eight MTG reaction zones or reactors in series. The product effluent gas from the final MTG reaction of the series is cooled from its final reaction temperature to about 100°F to recover its liquid hydrocarbon content separate from its C<sub>2</sub>- and C<sub>3+</sub> gaseous hydrocarbon content. At least a portion of C<sub>2</sub>- and/or C<sub>3+</sub> gaseous hydrocarbon by-product is recycled for use as a temperature moderating diluent gas for combination with fresh charges of alkoxy compound and the recovered liquid hydrocarbon is further refined into its various boiling point fractions for use as fuels or other purposes.

The combination of a fresh charge of alkoxy compound and C<sub>2</sub>- and/or C<sub>3+</sub> recycle gas with the product effluent gas from a preceding MTG reaction to form a combined gas of suitable inlet temperature (T<sub>1</sub>) and specific heat content as feed to a succeeding MTG reaction reduces the overall heat exchange duties with respect to the total make of hydrocarbon product by reducing the size of the heat exchangers needed for heating the fresh charge to the temperature to which the fresh charge of alkoxy compound and recycle gas must be preheated to condition it for admission to the succeeding MTG reactor, which mixture in line with its alkoxy content and its total specific heat content will react in contact with an MTG catalyst from a

-20-

temperature of  $T_i$  to the desired temperature  $T_R$  for the new reactor.

For example, conversion of 100 MPH of methanol (MeOH) creates a heat of reaction ( $Q_R$ ) of  $100 \times 24,000$  BTU/lb-mole MeOH = 2,400,000 BTU. To limit the temperature rise of the reaction gases to  $\Delta T_R = 75^\circ\text{F}$  for a gas inlet temperature  $T_i = 710^\circ\text{F}$  and an effluent gas outlet temperature  $T_R = 785^\circ\text{F}$  the total specific heat content of the feed gas must be  $2,400,000/75 = 32,000$  BTU/ $^\circ\text{F}$ . Hence recycle diluent gas is combined with this methanol in an amount to provide a total feed gas of this specific heat content. To preheat this total feed gas from its unit available temperature  $T_0$  of, say,  $100^\circ\text{F}$  to the reactor inlet temperature  $T_i$  of  $710^\circ\text{F}$  requires the addition of heat to such gas that is

$$(710-100) \times (32,000) = 19,500,000 \text{ BTU.}$$

On the other hand were a quantity of recycle diluent gas added to this methanol that would allow it to increase in temperature by  $150^\circ\text{F}$  due to the reaction of methanol, the total feed gas would have a total specific heat content of  $2,400,000/150 = 16,000$  BTU/ $^\circ\text{F}$ , meaning there would be less recycle diluent gas added. This feed gas could then react from a temperature of  $635^\circ\text{F}$  to a product gas of  $785^\circ\text{F}$ . Then to preheat this total feed gas stream from  $100^\circ\text{F}$  to  $635^\circ\text{F}$  would require the addition of heat of  $(635-100) \times (16,000) = 8,560,000$  BTU. By mixing this  $635^\circ\text{F}$  temperature gas having a specific heat content of  $16,000$  BTU/ $^\circ\text{F}$  with a gas stream having a temperature of  $785^\circ\text{F}$  and a specific heat content of  $16,000$  BTU/ $^\circ\text{F}$  a combined gas stream is formed having a temperature of  $710^\circ\text{F}$  and a total specific heat content of  $32,000$  BTU/ $^\circ\text{F}$ . Thereafter, reaction of the methanol content of this combined gas stream will increase the temperature of the gas by  $2,400,000/32,000 = 75^\circ\text{F}$  to provide an effluent gas stream having an outlet temperature  $T_R$  of  $785^\circ\text{F}$ .

As seen from the above, the quantity of heat exchange required for warmup of the feed gas is significantly reduced because the quantity of recycle diluent gas is

-21-

reduced, but the methanol is still converted in the same temperature zone, i.e., 710-785°F. Further, the efficiency with which the feed gas warm-up heat exchange is accomplished is significantly enhanced by reason of the increase in the differential temperature ( $\Delta T$ ) at which the heat exchangers performing this duty operate. On one hand, the 710°F warm-up situation would require a heat exchanger surface area ( $A_R$ ) of  $A_{R710} = 19,500,000 (1/P_{710})^{0.6}$  and the 635°F warm-up situation would require  $A_{R635} = 8,560,000 (1/P_{635})^{0.6}$ . The savings in heat exchange duties to be realized through the change in the differential temperature of heat exchange operations would only be offset if the difference in the pressure ( $P$ ) of the two operations were such that for the 635°F warm-up situation the pressure for operation was less than one-twelfth (1/12) that for operation of the 710°F warm-up situation. However, the change in the recycle GAS amounts between the two situations does not require such drastic reduction in the pressure of operation in order to maintain the same partial pressure of steam in the two product gases.

In these embodiments of the process of this invention wherein the first MTG reactor of the series operates on a feed gas composition that is preheated through adiabatic heat exchangers to the  $T_1$  temperature desired for its contact with the MTG catalyst therein, the heat exchange duty that this reactor contributes to the total heat exchange duty of the overall process is significantly greater in comparison to the quantity of methoxy equivalent converted therein than is that contributed to the total by the subsequent MTG reactors of the series. Hence, by using a larger number of reactor steps, the influence on the total heat exchange duties of the warmup for the first reactor is greatly reduced so that the benefit for the reduction in heat exchange for the subsequently added feed gas material is then almost totally available as the gain for this reaction choice. The number of reactors utilized together with the conditions chosen for their operation is

-22-

preferably such that no more than 20% of all alkoxy compound converted by the process is converted in the first reactor of the series, preferably no more than 10%. As made clear in the examples, the reduction of the total heat exchange duties in comparison to that for a single reaction stage processing of the same quantity of methoxy equivalent is substantial and can be as much as a reduction by about an order of magnitude of.

The heat exchange is further facilitated by using an alkoxy feed which will make a lower steam fraction and can therefore be used at higher pressure, which facilitates the heat exchange. Such feeds may be obtained by removing water from the alkoxy feed. Removing water from methanol is possible by distillation but that is a rather difficult operation. It is easier to remove steam from dimethyl ether, which can easily be made from methanol by contact at high temperature over an acid catalyst like alumina. The then unconverted methanol and most of the water present can easily be separated from the DME and recycled back to the DME conversion reactor. Use of the DME as the alkoxy feed for hydrocarbon production reduces the amount of water generated in the MTG reaction to only 0.5 mole water per mole of alkoxy equivalent, as against 1.3 for a methanol stream containing 30% of this methanol molar content as water.

Another means for increasing the efficiency of the heat exchange operations required is to employ a diluent gas composition containing low molecular weight species, like hydrogen, and/or species of a low specific heat value. Hydrogen for addition to the  $C_2$ - and/or  $C_3$ - diluent recycle gas can be provided out the methanol production unit by diffusion of the tail gas therefrom through a membrane preferential for permeation of  $H_2$  relative to other gas species. Further, use as a diluent gas of a recycle which is rich in the  $C_2$ - hydrocarbon by-product allows operations at a higher total pressure while providing for the same partial pressure of steam in the product gas than does a



-23-

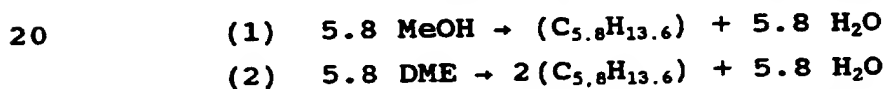
diluent gas rich in the C<sub>3+</sub> hydrocarbon by-production. The higher operational pressure provided by use of a C<sub>2</sub>- rich recycle provides for more efficient heat exchange of the feed and product gases by a factor of  $(1/P)^{0.6}$ .

5 With the process of this invention the operation of each MTG reactor in the series at the same inlet and outlet temperatures and at about the same partial pressure of steam at the outlet without significant changes of pressure therebetween becomes possible (i.e., allowing only for the  
10 pressure drop across each reactor needed for gas flow) -- thus providing for uniformity of product distribution production in each of the reactors. For example, with reference to use of dry methanol as the fresh alkoxy feed for each MTG stage, wherein the quantity of methanol feed  
15 doubles with each succeeding stage, when dry methanol is used as the first stage feed the partial pressure of water in the product gases of the early MTG stages is significantly lower than that of the later MTG stages. Hence, wherein the last MTG stage is operated at an outlet  
20 pressure that provides for a partial pressure of water of 2 ata, the first MTG stage operates at an outlet pressure that provides a partial pressure of water of about 1.015 ata. However, by adding water (steam) to the dry methanol feed to the first stage, and/or as needed or desired in the  
25 fresh methanol feed to later MTG stages, it is possible to operate each MTG reactor at substantially the same partial pressure of water at its outlet without significantly reducing the pressure at which the last MTG reactor operates. It is also possible, as desired, to operate a  
30 succeeding reactor at a condition of an inlet-outlet temperature or a pressure that significantly differs from the operating conditions of preceding reactors without exceeding a partial pressure of steam therein that would prematurely age or destroy its MTG catalyst content -- to  
35 permit the control of final product distribution, such as to minimize the durene content of the hydrocarbon product.

Nature of the Alkoxy Feed

-24-

Whatever the precise nature of the alkoxy feed, typically it will be available for use at about 100°F following its production and cooling to condense excess water from it. Although an MTG catalyst is active for production of hydrocarbon products with respect to any alkoxy compound -- i.e., alkanols, alkylethers, and combinations thereof -- and the process of this invention is applicable to the use of any suitable alkoxy compound; conventionally the alkoxy compound used is methanol, dimethylether, or equilibrium mixtures thereof produced by the catalytic dehydration of methanol. Hereafter, the process of this invention is described with respect to methoxy compounds -- i.e., methanol (MeOH), dimethylether (DME), and mixtures thereof (MeOH + DME). Further, reference to the amount of hydrocarbon products of which the methoxy compound is capable of production is referred to by its "methoxy equivalent." For example, for a hydrocarbon product having an average carbon number value of 5.8 carbon atoms, the following equations apply:



Hence, each mole of MeOH presents one methoxy equivalent and each mole of DME presents two methoxy equivalents.

Within the context of this invention the methoxy compound employed as feed may be methanol only, dimethyl ether only, or mixtures thereof together with such water vapor content as is normal to their production or, preferably, after water that is condensable at about 100°F has been separated therefrom. The nature of the methoxy composition selected as fresh feed to an MTG reactor affects the nature and/or quantity of diluent gas with which it must be combined for proper moderation of the temperature rise and water concentration control within an MTG reactor. On a methoxy equivalent basis, each mole of MeOH releases a greater quantity of heat (24,000 BTU/lb-mole) and H<sub>2</sub>O by-product (1 mole H<sub>2</sub>O/mole) than does DME (1/2 mole H<sub>2</sub>O/mole and 35,200 BTU/lb-mole). Further, since

-25-

the specific heat of MeOH (16.94 BTU/°F/lb-mole) and DME (25.08 BTU/°F/lb-mole) differ, the composition of the methoxy feed selected influences the degree to which the methoxy + recycle diluent gas composition must be preheated before its admixture with the product effluent gas from a preceding MTG reactor to yield a combined gas stream of suitable temperature and specific heat content for feeding to a succeeding MTG reactor.

An ideal case for purposes of achieving the greatest economics in the overall heat exchange requirements for the hydrocarbon production process is that of exclusive use of DME as the methoxy compound. Next in order of preference is that of the use of a dehydration equilibrium mixture of MeOH + DME as the methoxy feed.

#### The MTG Catalyst

A variety of compositions have been disclosed as suitable catalysts for the conversion of methoxy compounds to hydrocarbon compounds, as for instance in U.S. Patent Nos. 3,702,886; 3,709,979; 3,832,449; 3,998,889, 4,076,842; 4,016,245 and 4,046,859, the disclosures of which are herein incorporated by reference. Further, this invention is applicable to any composition now existing or which may be developed which catalyzes the conversion of alkoxy compounds to hydrocarbon products, especially wherein the catalyst composition exhibits a similar sensitivity to temperature and water concentration in terms of its activity and aging characteristics as now existing MTG catalyst compositions do.

Whatever MTG catalyst composition is selected for use, for essentially complete conversion of the methoxy compound to hydrocarbon to occur, the methoxy containing feed gas must first be conditioned to have about at least a minimum inlet temperature ( $T_I$ ) of about 650°F, and preferably about 700°F. Further, the feed gas should have a specific heat content that limits the temperature increase ( $\Delta T_R$ ) between the inlet temperature ( $T_I$ ) and outlet temperature ( $T_R$ ) of the MTG reactor to less than 100°F, preferably 85°F or less.

-26-

The inlet gas temperature may range from about 650 to 720°F to insure complete conversion, while the outlet temperature should be limited to a range of from about 730-800°F. To prevent premature aging or damage of the MTG catalyst a temperature of 800°F should not be exceeded. Also, the partial pressure of steam at the outlet should be limited to a range of 1.85 to 2.2 ata, and preferably 1.95 to 2.15 ata.

Within the broad ranges of inlet and outlet temperature, various narrower ranges are preferred for purposes of product composition and distribution. For example, the amount of durene -- an undesirable hydrocarbon component for purposes of fuel uses -- has been found to vary with the reaction temperature, increasing with lower reaction temperatures and decreasing with higher temperatures. Accordingly, to minimize durene content while maximizing the fraction of liquid hydrocarbon and the octane value of the liquid hydrocarbon fraction an inlet temperature of at least about 700°F is preferred. To further insure against premature catalyst aging or destruction a temperature of 785°F and partial pressure of steam of 2.2 ata at the reactor outlet is preferably not exceeded.

The improved process is based on adiabatic reaction in a multiple reactor system with intermediate injection of colder feed. While the different reactors can easily operate under different conditions, it is easier to explain the new process and its advantages by discussing the special case of all reactor steps operating under similar conditions as to the temperature zone for the contact with the catalyst and the final steam vapor pressure of the reactants in each reactor.

As a typical set of conditions by which to illustrate practice of the process of this invention, unless otherwise indicated, for each reactor in the series a gas stream inlet temperature of 710°F is used and the gas composition for feed thereto is chosen to provide for a  $\Delta T_R$  of 75°F for

-27-

an outlet gas of 785°F at an outlet pressure that provides for a partial pressure of steam of approximately 2 ata. The methoxy feed for each is MeOH, DME, or a mixture thereof as indicated and is as available for use at a  
5 temperature of 100°F. The diluent recycle gas is a C<sub>2</sub> and C<sub>3+</sub> gaseous hydrocarbon product of the MTG process or a mixture thereof in a molar ratio that provides a lb-mole quantity thereof to have a specific heat content as indicated. Further, specific heat values of the various  
10 components of the involved gas streams are utilized for calculations of the specific heat contents of these gas streams as given in the text which follows. The precise numerical values of these specific heat values may vary somewhat in actual practice with variations in the precise  
15 compositions of the components and/or the temperature and pressures to which they are actually subjected, as will be appreciated by those skilled in the art. As desired, in putting this invention into actual practice, one skilled in the art may without undue experimentation determine more  
20 precise and accurate numerical values for the circumstances of the actual application. Nevertheless, this would but slightly alter the precise numerical values given hereafter in the discussion of results of the use of this invention, but will not significantly affect the general conclusions  
25 discussed about the results and benefits to be had from a practice of this invention.

#### The Fresh Feed Composition

The composition of fresh feed to be added to a product effluent gas from a preceding MTG reaction to form a  
30 combined gas to be fed to a succeeding MTG reaction may be conceptually viewed as comprising two components which in sum equal the fresh feed composition. The first component of the fresh feed is that amount of alkoxy compound that is required to heat up the product effluent gas composition by  
35 the delta ( $\Delta$ ) between T<sub>R</sub> and T<sub>I</sub> ( $\Delta T_R$ ) desired to be achieved in the succeeding MTG reaction. The second component is that quantity of alkoxy plus recycle diluent composition

-28-

which by itself would react with a  $\Delta T_R$  desired for the succeeding MTG reaction (hereafter this component is referred to as the " $\Delta T_R$  balanced alkoxy-recycle diluent composition"). When summed, the first and second  
5 components provide for a total fresh feed having a total specific heat content that will cool down the effluent gas by heating up the fresh feed to form a combined gas of the temperature desired as the inlet temperature ( $T_I$ ) for admission to the succeeding MTG reaction. This in turn  
10 then dictates the temperature to which the fresh feed must itself be preheated ( $T_p$ ) before being mixed with the product effluent gas which is at its reaction temperature ( $T_R$ ) to form the combined gas at temperature  $T_I$  that upon reaction in a succeeding MTG zone will increase in  
15 temperature by  $\Delta T_R$  to yield a new effluent gas of an outlet temperature as desired,  $T_R$ .

Wherein one has two gas streams, each being at the same temperature, say  $T_R$ , then upon mixture of one with the  
20 other a combined gas stream of the same temperature  $T_R$  is obtained. However, if one takes one gas stream that has already reacted its alkoxy content to reach a temperature of  $T_R$  and another gas stream which is at a temperature  $T_p$  from which by reaction of its alkoxy content would reach a  
25 temperature of  $T_R$  and mix the hot with the cooler gas stream a combined gas stream is obtained having a temperature  $T_I$  which is less than the  $T_R$  of the hot gas stream but greater than  $T_p$  of the cooler gas stream. Thereafter the reaction of the alkoxy content of this  
30 combined gas stream will elevate its temperature to  $T_R$ ; this because each of the component parts of this combined gas stream -- the hot and the cooler gas streams -- were either once at the temperature  $T_R$  or by reaction of its alkoxy content would be elevated to the temperature  $T_R$ .  
35 The temperature  $T_I$  that is obtained upon mixing of the two gas streams is related to the specific heat content of each, which in turn is related to the composition and

-29-

quantity of each. Each molecular species comprising either gas stream has a specific heat value in terms of the heat (BTU) required to elevate its temperature ( $^{\circ}\text{F}$ ) per a unit quantity (lb-mole) of that species. Herein, specific heat values are given in terms of BTU/ $^{\circ}\text{F}$ /lb-mole, meaning the number of BTUs required to elevate one lb-mole of that material by one  $^{\circ}\text{F}$ . The specific heat content of a gas stream is then the number of BTUs required to elevate that gas stream by one  $^{\circ}\text{F}$ , and this specific heat content is the sum of the specific heat value of a species times its quantity for each species contained in the gas stream.

Thus, for example, for methanol ( $Q_R = 24,000$  BTU/lb-mole) to condition it for reaction to hydrocarbon products such that the temperature increase due to its reaction is  $75^{\circ}\text{F}$  ( $\Delta T_R$ ) requires that the specific heat content of the feed gas containing this one lb-mole of methanol be  $24,000/75 = 320$  BTU/ $^{\circ}\text{F}$ . The one lb-mole of methanol itself contributes 16.94 BTU/ $^{\circ}\text{F}$  of this specific heat content, leaving 303.06 BTU/ $^{\circ}\text{F}$  of this content to be satisfied by other components, namely the diluent recycle gas comprising  $\text{C}_2$ -,  $\text{C}_{3+}$ -, steam, hydrogen or mixtures thereof. For discussion purposes the following specific heat values for such recycle components are assumed;  $\text{C}_2$ - hydrocarbon gas, 13.16 lb BTU/ $^{\circ}\text{F}$ /lb-mole;  $\text{C}_{3+}$  hydrocarbon gas, 36.0 BTU/ $^{\circ}\text{F}$ /lb-mole; steam, 8.8 BTU/ $^{\circ}\text{F}$ /lb-mole; hydrogen, 8.0 BTU/ $^{\circ}\text{F}$ /lb-mole. Selecting a 3:1 molar ratio of  $\text{C}_2$ :- $\text{C}_{3+}$  hydrocarbon gas as the diluent, this recycle mixture has a specific heat value of  $[(3 \times 13.16) + (36.0)]/4 = 18.87$  BTU/ $^{\circ}\text{F}$ /lb-mole. Then 16.0604 lb-moles of this 3/1 recycle diluent gas would be required for each 1 lb-mole of methanol to form a feed gas that would react with a temperature increase of  $75^{\circ}\text{F}$ . This  $\Delta T_R = 75^{\circ}\text{F}$  balanced gas composition would then be:

$\text{CH}_3\text{OH} = 1.00$  lb-mole,

Recycle (3/1) = 16.064 lb-mole,

Specific Heat Content = 320 BTU/ $^{\circ}\text{F}$ .

This feed as first preheated to  $710^{\circ}\text{F}$  when contacted with an MTG catalyst will react to form a product gas having a

-30-

temperature of 785° and a specific heat content which, for discussion purposes, is assumed to be the same as the feed gas from which it was formed, namely 320 BTU/°F.

5 This hot product gas at 785°F has a content of heat in excess of that at which it would otherwise have a temperature of 710°F of 24,000 BTU, which is the heat released by reaction of the methanol from which the product gas stream was formed. Transfer of this 24,000 BTU of heat from this product gas stream to another medium will reduce  
10 the temperature of this product gas stream from its 785°F temperature to a temperature of 710°F. The medium of transfer can be a cooler gas stream, and the transfer can be accomplished by indirect exchange as through the heat transfer surfaces of an adiabatic heat exchanger or by  
15 direct gas-to-gas contact by admixture of the two gases.

In this invention the transfer of this excess product heat to the cooler feed gases is in part accomplished through adiabatic heat exchangers -- to preheat a fresh feed gas charges to a temperature  $T_p$  -- and in part by  
20 direct gas-to-gas contact -- to finally warm up the preheated fresh feed gas charges from its  $T_p$  preheat temperature to a temperature  $T_i$  desired for contacting it with a MTG catalyst. The direct gas-to-gas heat exchange is first accomplished, and the product gas from the last of  
25 the MTG reactions in series is used for indirect heat exchange through adiabatic heat exchangers to warm up the fresh feed gases to their preheat  $T_p$  temperature.

As to the direct gas-to-gas heat exchange to warm up a fresh feed gas from its preheat temperature  $T_p$  to the  $T_i$   
30 temperature desired for its contact with an MTG catalyst, the specific heat content of the fresh feed gas governs how much it can be warmed up by the cooling down from  $T_R$  of the hot product gas with which it is mixed to a temperature  $T_i$ . The amount by which the fresh feed gas will be warmed  
35 up ( $T_i - T_p$ ), while the product gas is cooled down ( $T_R - T_i$ ) is related to the ratio of the specific heat content of the



-31-

fresh feed gas ( $S_f$ ) to the specific heat content of the product gas ( $S_p$ ) according to the equation:

$$S_f = \frac{(T_R - T_I)}{(T_I - T_P)} \times (S_p).$$

For the case under discussion, wherein it is desired to have the next reaction begin at a temperature of  $T_I = 710^\circ\text{F}$ , the composition and quantity of the new feed gas are governed then by

$$S_f (710 - T_P) = 24,000,$$

and its specific heat content is a function of the temperature to which it is preheated before admixture with the hot product gas. Selecting then, for discussion purposes, a feed gas preheat temperature of  $635^\circ\text{F}$  ( $T_P$ ), the specific heat content of the fresh feed must equal that of the product gas with which it is to be mixed, and the combined gas stream will have a specific heat content that is the sum of its component parts. To then have this combined gas stream react to a new product gas temperature  $T_R = 785^\circ\text{F}$  requires that it contain a quantity of alkoxy compound, here for discussion purposes, methanol, to heat its now doubled specific heat content of  $640 \text{ BTU}/^\circ\text{F}$  by  $75^\circ\text{F}$ , or  $640 \times 75 = 48,000 \text{ BTU}$ . This quantity of heat is supplied through the reaction of 2 lb-moles of methanol ( $Q_R = 24,000 \text{ BTU/lb-mole}$ ) which contributes  $33.88 \text{ BTU}/^\circ\text{F}$  towards the needed  $320 \text{ BTU}/^\circ\text{F}$  specific heat content required for the new feed gas, leaving  $286.12 \text{ BTU}/^\circ\text{F}$  of the heat content to be supplied by diluent gas. Where this remaining quantity is supplied by a diluent gas comprising a 3/1 molar ratio of  $\text{C}_2\text{:C}_3+$  hydrocarbon gas, then  $15.1627 \text{ lb-moles}$  of such recycle gas is required. Hence the composition of the fresh feed gas would be:

$$\text{CH}_3\text{OH} = 2.00 \text{ lb-mole},$$

-32-

Recycle (3/1) = 15.1627 lb-mole,  
Specific Heat Content = 320 BTU/°F

Reaction of the combined gas mixture will then produce a new product gas having a temperature of 785°F and a specific heat content of 640 BTU/°F.

This new product gas ( $T_R=785^\circ\text{F}$ ;  $S_P=640$  BTU/°F) may be used as the hot gas source for mixture with a new portion of fresh feed gas to form a combined gas mixture for another reaction over an MTG catalyst between any reaction temperature zone of  $T_I$  to  $T_R$  as may be desired.

Take for instance that for this next reaction it is desired to contact the next MTG catalyst at a temperature  $T_I = 700^\circ\text{F}$  and have a new product gas temperature from that reaction limited to 740°F. In this case the previous product gas requires cool down from 785°F to 700°F for a  $T_R - T_I$  of 85°F, meaning the previous product gas must give up  $640 \text{ BTU/}^\circ\text{F} \times 85^\circ\text{F} = 54,400$  BTU of heat which is then available for warm up of the new feed gas to the desired inlet temperature of 700°F. Once this previous product gas component has been cooled to 700°F, at its specific heat content of 640 BTU/°F, to increase its temperature to the  $T_R = 740^\circ\text{F}$  desired for the new product gas requires  $640 \text{ BTU/}^\circ\text{F} \times 40^\circ\text{F} = 25,600$  BTU of heat to be released by reaction of methanol contained in the new feed charge. To this end, after reaction by methanol has warmed itself or its reaction product up by 40°F to consume  $16.94 \times 40 = 677.6$  BTU of the heat of its reaction, there remains  $24,000 - 677.6 = 23,322.4$  BTUs of heat to warm up the previous product gas, thus  $25,600/23,322.4 = 1.06667$  lb-mole methanol are required to reheat the previous product gas from 700 to 740°F. If again the new feed gas has been preheated to a  $T_P$  temperature of 635°F the composition and quantity of the new feed gas is governed by

$$S_F (700 - 635) = 54,500$$

or its  $S_F$  required is 836.923 BTU/°F of which 18.594 BTU/°F is provided by the methanol required to reheat the previous product gas that will become part of the combined gas

-33-

stream to be reacted. Hence, 818.329 BTU/°F of value remains to be filled in the new feed gas by methanol and recycle constituents and these constituents must react from a  $T_1$  temperature of 700°F to the new temperature desired of 740°F. Here, to moderate the reaction of one lb-mole methanol to a 40°F increase in temperature upon its reaction requires a specific heat content of  $24,000/40 = 600$  BTU/°F, of which that one-lb-mole of methanol contributes 16.94 BTU/°F, leaving 583.06 BTU/°F of content to be supplied by a recycle diluent gas. Again, using a 3/1  $C_2:C_3$  recycle gas diluent would require 30.8988 lb-mole of such diluent. Hence, the  $\Delta T_R=40^\circ\text{F}$  balanced gas composition would be:

CH<sub>3</sub>OH - 1.00 lb-mole,  
 Recycle (3/1) - 30.8988 lb-mole  
 Specific Heat = 600.0 BTU/°F.

To supply the 818.329 BTU/°F needed, 1.36388 times this quantity of the  $\Delta T_R = 40^\circ\text{F}$  balanced gas composition is needed. Hence the new feed gas would be:

	Component To Reheat Previous Product Gas	$\Delta T_R=40^\circ\text{F}$ Balanced Composition x 1.36388	New Feed Gas
CH <sub>3</sub> OH	1.097657	1.36388	2.461538
Recycle	-0-	42.14231	42.14231
Specific Heat Content	18.594	818.329	836.923

It should be clear from the general discussion given above that in order for the new process to effect significant savings in heat exchange the above mentioned  $T_p$  temperature of the added feed should be significantly lower than the  $T_1$  temperature of inlet to the reactor obtained after addition of the hot exit gas from the earlier reactor. The given examples clearly demonstrate that a reduction of about a factor of 2 can be obtained with as little as 60°F difference between these two temperatures. It is, however, preferred to use a more optimal temperature

-34-

difference of about 200°F and a larger number of reactors, like 10, preferably 5 to 8, so that a more sizeable heat exchange duty reduction of about one order of magnitude can be obtained, especially when using DME only.

5        It should be understood that especially when using a larger number of reactors, the resulting pressure drop may begin to exert a negative effect on the size of the heat exchanger. This has been taken into account in calculation of the advantages to be obtained.

10        Accordingly, to maximize the efficiency of heat exchange operations (which is a variable of pressure and the volume of gas treated for heat exchange) while also maximizing the saving required for fresh feed preheating and/or product gas cooldown for product recovery the  
15        following conditions are preferred:

- (1) preheating of the fresh feed gas to a temperature within 75 to 260°F of the  $T_1$  temperature selected for admission of the combined gas stream to the succeeding MTG reaction zone, preferably to  
20        within 100 to 210°F, and more preferably to within 100 to 160°F;
- (2) formation of the combined gas stream to have a temperature  $T_1$  from 650-720°F, and preferably from about 675-720°F;
- 25        (3) selection of the alkoxy content of the fresh feed stream to have a heat of reaction content that, upon reaction of that alkoxy content thereof, would increase the temperature of the combined gas stream by a  $\Delta T_R$  of 10-150°F, preferably by 30-  
30        120°F, more preferably by 50-100°F and most preferably by 50-85°F; and
- (4) formation from reaction of the combined gas stream in the succeeding MTG reaction zone of a new effluent gas having a temperature  $T_R$  of from  
35        about 700 to 800°F, preferably from about 730 to 800°F, and more preferably of from about 750 to 785°F.

-35-

Reactor Sequence

Figure 1 illustrates one embodiment of the process which employs five MTG reactors in series flow, reactors 10, 20, 30, 40 and 50. A methoxy feed with an appropriate amount of water to allow initiation of reaction over the MTG catalyst together with an appropriate amount of recycle diluent gas at 100°F, is fed by line 2 to heat exchange 3 and is there preheated to 710°F then fed by line 4 to the inlet of reactor 10 and passed into contact with an MTG catalyst. The product effluent gas is passed by line 11 to line 12. A fresh quantity of methoxy feed at 100°F passes from line 5 through heat exchanger 6 and is preheated to a temperature  $T_p$  and then passed by line 7 through metering valve 7a into admixture with the product effluent gas in line 12. A further quantity of recycle diluent gas 5a at 100°F passes through heat exchanger 8 and is preheated to temperature  $T_p$ , then passed by line 9 through metering valve 9a into admixture with the product effluent gas and methoxy feed in line 12. The combined gas stream passes from line 12 into contact with the MTG catalyst in reactor 20 and the product effluent gases pass therefrom by line 13 into line 14 where the product effluent gas becomes admixed with a further quantity of methoxy feed and recycle diluent gas, each at temperature  $T_p$ , as metered into line 14 through valves 7b and 9b respectively. Again, the product effluent gas from reactor 30 passes by line 15 into a further quantity of methoxy and recycle gases each at  $T_p$ , as metered in through valves 7c and 9c respectively, and the combined gases pass by line 16 into contact with an MTG catalyst in reactor 40. The product effluent gas from reactor 40 passes by line 17 into mixture with a further quantity of methoxy and recycle diluent gas at  $T_p$ , as metered in through valves 7d and 9d respectively and the combined gases pass by line 18 into contact with an MTG catalyst in reactor 50. The product effluent gas from reactor 50 passes by line 19 to subsequent processing units where it is cooled to 100°F for separation and recovery of its various components, such

-36-

as its  $C_2$ - and  $C_3$ - hydrocarbon content for recycle use as a diluent gas, its liquid hydrocarbon content to be processed into its fuel grade fractions, and its water content.

#### Heat Exchange Requirements

5 In the process of converting an alkoxy compound to hydrocarbon products by contact with an MTG catalyst it is necessary to heat up feedstocks of alkoxy-diluent gases from their unit available temperature ( $T_0$ ) to a temperature at which they will react over an MTG catalyst, namely  $T_1$ .  
10 By reason of the exothermic reaction of the alkoxy compound to hydrocarbon product the product effluent gas resulting from contact with an MTG catalyst has an even higher temperature,  $T_R$ . To recover the hydrocarbon product from the reaction gases, it is necessary to cool the product  
15 effluent gas from its temperature  $T_R$  to a temperature at which its normally liquid hydrocarbon content condenses, typically about 100°F.

Typically, the product gases at  $T_R$  and feedstock gases at  $T_0$  are passed through adiabatic heat exchangers wherein  
20 heat content  $Q$  is exchanged between the product gases and feedstock gases through a heat exchange surface that separates these gas streams, whereby the product gases cool down in temperature to the extent they transfer a content  $Q$  of their heat to the feedstock gases which are thereby  
25 increased in temperature.

In an ideal case, the product gas contains a quantity of heat  $Q$  that is in excess of that quantity required to heat up the feedstock gases to  $T_p$  by an amount that is equal to the heat released by the alkoxy compound that  
30 reacted to form the product gases. Thus, following the first heat exchange between the product gases at  $T_R$  and feedstock gases at  $T_0$  through the heat exchange surface of an adiabatic heat exchanger, the feedstock gases are heated up to  $T_p$  and the reaction gases are cooled down to a  
35 temperature  $T_x = T_R - (T_p - T_0)$ . Hence, to recover normally liquid hydrocarbon compounds from the reaction gases it is necessary to cool them further from their  $T_x$  temperature to

-37-

about 100°F, which is typically the temperature  $T_0$  at which the feedstock gases are available since a major portion of the feedstock gases are the  $C_2$ -and/or  $C_3$ + hydrocarbon by-products recovered from the reaction gases and used as the recycle or diluent component of a feedstock. In this last step of reaction gas cooling, the reaction gases at  $T_x$  are heat exchanged in an adiabatic heat exchanger operating with chill water, typically at a chill water temperature of 70°F.

With the process of this invention it is possible to realize significant economies in the heat exchange requirements in terms of the size of the heat exchangers required for feedstock heatup duties and the heat exchangers required for the final step of reaction gas cooldown for hydrocarbon product recovery.

For example, on the basis of methoxy equivalent processed to hydrocarbon product, using as the standard for comparison a process comprising a single reactor pass of the same quantity of methoxy compound for conversion to hydrocarbon product at a reactor inlet temperature of 710°F, and outlet temperature of 785°F and at an outlet pressure that provides for a partial pressure of water of 2.15 ata and wherein the feedstock gases are available at 100°F and the recycle diluent gas comprises a 1:3 molar ratio of  $C_3$ +: $C_2$ -hydrocarbon by-product gas, Figures 2 and 3 illustrates the affect on the size of the heat exchangers based upon the relative heat exchange surface area ( $A_R$ ) required for feedstock heating.

Figure 3 is for methanol containing 0.35 moles water per mole of methanol as feed, Figure 2 is for dry DME as feed.

Figures 2 and 3 indicate the results of a series of calculations based on assuming the maximum allowable pressure in the second reactor, reactor II, which is the first reactor with a low amount diluent recycle gas in the feed. From then on a pressure drop per reactor stage of 0.35 ata is taken. The final pressure out of the last

-38-

reactor is taken as guidance for the size of the relative heat exchanger surface area necessary for warmup of the feeds. The heat exchanger for the feed of the first reactor, reactor I, is separately sized from the combined heat exchanger for the combined cold feed. For all  
5 reactors in both cases a temperature of reaction is chosen, starting at 710 and ending at 785F. The added feed is fed in at a series of preheat temperatures  $T_p$ , varying in steps of 50°F from 100 to 650°F. The figures clearly show a  
10 minimum for the relative heat exchange surface area, that varies with the number of reactor steps used. The minimum seems to be at about the same temperature independent of the nature of the methoxy feed. For both feeds considered, the minimum is at a preheat temperature  $T_p$  of about 550°F  
15 for five reactors and slowly decreases to about a rather flat minimum at  $T_p = 450^\circ\text{F}$  with the use of ten stages.

For comparison it should be noted that a one reactor approach as applied to methanol with 0.35 mole of water per mole of methanol requires a heat exchange surface area of  
20 about 325.4 relative units on the basis of a pressure of operation of 22.06 ata resulting from the chosen feed. With the same feed the present system with ten stages reduces this heat exchange surface area number to 42.6 relative units while use of DME reduces it further down to  
25 28.5 relative units.

The conclusion is therefore that the process of this invention reduces the required heat exchange surface area for feed gas warm-up between 8 and 10 fold.

As may also be realized, in the process of this  
30 invention the use of a recycle diluent gas of a low specific heat content as a feedstock component is preferred to that of a diluent gas of a high specific heat content. As the  $C_2$ - content of a diluent recycle gas increases at the expense of its  $C_3$ - content while the specific heat  
35 content of the diluent gas remains the same, then the quantity of diluent recycle gas increases and constitutes a larger volume of the final product gas. This in turn



-39-

means that the water by-product content of the final product gas becomes a small fraction of the total gas content and the gas can be processed at a higher pressure while still maintaining its water content at the same steam partial pressure. For example, where MPH means mole-per-hour, to react 1 MPH methanol ( $\text{CH}_3\text{OH}$ ) to a hydrocarbon product with a temperature rise of the gas stream limited to 75°F requires a feed gas composition having a specific heat content of 320 BTU/°F. Of this amount the methanol itself contributes 16.94 BTU/°F leaving 303.06 BTU/°F to be supplied by a diluent recycle gas. If supplied solely by a  $\text{C}_{3+}$  recycle gas then 8.42 MPH  $\text{C}_{3+}$  recycle would be required and the final product gas would comprise 8.42  $\text{C}_{3+}$  recycle, 1 MPH  $\text{H}_2\text{O}$ , and 0.1724 MPH hydrocarbon product and a total pressure of 19.18 ata would produce a steam partial pressure of 2.0 ata. On the other hand, if the remainder of the specific heat content required were supplied solely by a  $\text{C}_2$ - recycle then 23.03 MPH  $\text{C}_2$ - recycle would be required and the final product gas would comprise 23.03 MPH  $\text{C}_2$  recycle, 1 MPH  $\text{H}_2\text{O}$  and 0.1724 MPH hydrocarbon product. At a pressure of 48.40 ata such gas composition would have a steam partial pressure of 2.0 ata. Of the two gas compositions discussed, that using the  $\text{C}_2$ - recycle is more efficiently heat exchanged because of its processing at the higher pressure, in relative terms, requiring only about 57.4% of the heat exchange surface area as would otherwise be required by the gas composition using a  $\text{C}_{3+}$  recycle. However, the  $\text{C}_{3+}$  hydrocarbon by-product steam contains olefins and use of a  $\text{C}_{3+}$  recycle promotes further reaction of the olefin content thereof to  $\text{C}_{5+}$  hydrocarbons, increasing the yield of the gasoline grade hydrocarbon product. Hence, a reasonable amount of  $\text{C}_{3+}$  content in the diluent recycle gas is generally desirable. Accordingly, use of the  $\text{C}_2$ - hydrocarbon by-product (specific heat about 13.16 BTU/°F/lb-mole) and diluent gases rich in  $\text{C}_2$ -compared to  $\text{C}_{3+}$  hydrocarbon by-product, on the order of a  $\text{C}_2$ :- $\text{C}_{3+}$

-40-

molar ratio of from about 3:1 to about 1:3, as the diluent gas component of a feedstock is preferred.

The preference with respect to the number of reactors in a series and the fresh alkoxy recycle diluent feed preheat temperature are somewhat interrelated. Given the fact that to maintain gas flow through the reaction train a pressure drop must be allowed across each reactor, the number of reactors in a series at which a maximum savings in heat exchange duties per methoxy equivalent converted is limited by this pressure drop factor since lower pressure means lower heat exchange efficiency.

Generally, the maximum in heat exchange economies are realized in the range of fresh feed preheating of about  $T_p = 400$  to  $550^\circ\text{F}$ . Within this range the number of MTG reactors required to realize the maximum in heat exchange required may vary from about 5 to about 10 reactors. In a five reactor series the maximum in heat exchange economy is realized with a preheat of the fresh feeds to about  $550^\circ\text{F}$ ; whereas with a fresh feed preheat to  $500^\circ\text{F}$ , the maximum in heat exchange economy is realized in the last of a series of six to eight reactors; and at a preheat of  $450^\circ\text{F}$  the maximum economy is realized in the last of a series of nine to ten reactors. On the basis of total methoxy equivalent converted, compared to the relative heat exchange surface area required for feed gas warm-up for conversion in a single reactor pass; in accordance with this invention with a fresh feed gas preheat of  $550^\circ\text{F}$  with a five reactor series requires only about 26.8% of the heat exchange surface area; for a series of six to eight reactions with a fresh feed preheat to  $500^\circ\text{F}$  only 22.1 to 16.3% of the heat exchange surface area is, respectively, required; and for a series of nine to ten reactors with a preheat of 450 only 14.5 to 13.1% of the heat exchange surface area is required.

#### Product Compositional Control

For purposes of influencing the hydrocarbon distribution of the product in favorable ways, it is

-41-

possible with the process of this invention to tailor the conditions of inlet-outlet temperature and effluent gas steam partial pressure of water for any reactor in the series to a set of conditions different than other reactors in the series. For example, durene (1,2,4,5 tetramethyl benzene) is not a desirable hydrocarbon component of the product whereas toluene and xylene ("TX" octane boosters) are desirable hydrocarbon components. To minimize the durene and maximize the TX components of the hydrocarbon product, it may be desirable to operate the early reactors in the series at a higher inlet temperature condition (i.e.  $T_I \geq 720^\circ\text{F}$ ) to decrease aromatic hydrocarbon production therein while operating the last reactor(s) at a lower inlet-outlet temperature condition (i.e.,  $T_I = 700$ ,  $T_R \geq 760^\circ\text{F}$ ) to increase aromatic production, but limit or reduce over methylation of the aromatics to durene and/or trimethyl benzene, providing all reactors are operated at a similar partial pressure of water outlet value.

#### The Recycle Diluent Gas Hydrogen Content

As mentioned before, heat exchangers operate more efficiently at higher rather than lower pressures. As a rule of thumb heat exchange is enhanced by the factor of pressure (P) to the power 0.6. The relative surface area needed therefor is related to pressure by the factor  $(1/P)^{0.6}$ . Further, with respect to the heat exchange of gases, exchange is more efficient as to species of lower molecular weight than of higher molecular weight. Hence to further enhance the efficiency of heat exchange operations it is preferred to utilize as a diluent gas composition one which incorporates a percentage of hydrogen (specific heat about 8 BTU/ $^\circ\text{F}$ /lb-mole) ranging from about 10 to about 50 mole% hydrogen and more preferably from about 15 to about 30 mole % hydrogen.

#### First Reactor Recycle Operation

In another embodiment of the invention the heat exchange duties required for conversion of alkoxyl compound to methanol may be even further reduced by operating the

-42-

first MTG reactor in a mode wherein a portion of its produce effluent gas is recycled back to its inlet for combination with fresh alkoxy-diluent recycle feedstock admitted thereto.

5           This mode is illustrated in Figure 4, wherein feed gas preheated to a temperature  $T_p$  is routed by line 70 to the inlet 72 of MTG reactor 74. Product gas at a temperature  $T_R$  is taken from reactor 74 by line 76 and is then split into two product streams, one of which proceeds through  
10 line 80 to the next MTG reactor in the series (not shown) and the other product gas portion is routed by line 78 to a hot gas fan 82 wherein it is recompressed to a pressure equal to that of the feed gas to MTG reactor 74 and then routed by line 84 for addition to reactor inlet 72 in  
15 admixture with feed gas routed to the inlet 72 via line 70. In this mode, as illustrated by Figure 4, the alkoxy-diluent recycle feedstock would be preheated to a preheat temperature  $T_p$  and upon combination with the recycle portion of the product stream at  $T_R$  would form a combined  
20 gas stream of temperature  $T_i$  for contact with the MTG catalyst. In this mode of operation the composition of the alkoxy-diluent recycle feedstock is adjusted to provide an amount of alkoxy compound relative to the diluent recycle content of this feed that upon reaction to hydrocarbon  
25 product provides a heat of reaction that raises the temperature of the combined gas stream from  $T_i$  to  $T_R$ . Otherwise stated, the quantity of alkoxy compound relative to the diluent recycle content of the feed is that which by heat of reaction would increase the temperature of the feed  
30 alone from its preheat temperature  $T_p$  to  $T_R$ .

          This product recycle mode of operation for the first MTG reactor means that preheating of the feedstock gases can more efficiently be accomplished, i.e., a smaller heat exchange area is required, because the differential heat  
35 exchange temperature  $\Delta T$  as reflected in the heat exchange factor  $(1/\Delta T)$  is now

-43-

$T_R - T_P$  rather than  $T_R - T_I$ . To accomplish this product recycle requires a slight recompression of this portion of the product gas from its reactor outlet pressure ( $P_0$ ) to the gas pressure required for the reactor inlet ( $P_I$ ), in other words, to compensate for the pressure drop occurring across this reactor. This may readily be accomplished with a hot fan, a conventional item of equipment. However to utilize a conventional hot fan for this recompression, the volume of product recycle that can be accomplished is limited by the fan capacity and this in turn will generally set the preference for the conditions to be employed in the subsequent MTG reactors in the series. That is, for a given total of gasoline production desired, once the capacity of the first reactor product recycle is determined, the most optimum of conditions for subsequent feed preheat temperature and the number of MTG reactors may be selected for the balance of the desired gasoline production.

#### EXAMPLES

The following examples illustrate operations in accordance with the process of the invention and, in some cases, for comparison purposes illustrate operations in accordance with prior art practice. Unless otherwise indicated the following values were applied in preparation of the examples.

#### Heat of Reaction

- (1) Dimethylether (DME)  $\rightarrow$  (2/5.8) hydrocarbons +  $H_2O$   
(35,200 BTU/lb-mole DME)
- (2) Methanol (MeOH)  $\rightarrow$  (1/5.8) hydrocarbons +  $H_2O$  (24,000  
BTU/lb-mole MeOH)

-44-

	<u>Specific Heats</u>	<u>BTU/°F/lb-mole</u>
	(1) DME	25.08
	(2) MeOH	16.94
	(3) H <sub>2</sub> O	8.8
5	(4) C <sub>2</sub> - recycle gas	13.16
	(5) C <sub>3+</sub> recycle gas	36.0
	(6) Hydrocarbon Product	47.212
	(7) H <sub>2</sub>	8.0

10 Operations in accordance with the proposed invention  
 in comparison to that for a single reactor pass method of  
 converting the same quantity of methoxy equivalent is  
 discussed below. In each of Example 1 to 5, unless  
 otherwise indicated, the effluent gas temperature at the  
 15 outlet (T<sub>R</sub>) of each MTG reactor is 785°F, the inlet gas  
 temperature (T<sub>I</sub>) of the gas feeds to each MTG reactor is  
 710°F, and the partial pressure of steam in the effluent gas  
 of each MTG reactor is 2.15 ata. A pressure drop of 0.35  
 ata across each MTG reactor is assumed. Example 1 is a  
 20 comparative example and illustrates the conversion of the  
 methoxy component of the feed gas by a single pass through  
 one reactor. Examples 2 to 5 illustrate the conversion of  
 a similar quantity of methoxy component in a series of five  
 MTG reactors operating in accordance with the process of  
 25 this invention. The relative heat exchange surface area  
 (A<sub>R</sub>) required for feed gas warm-up in the examples is  
 calculated according to the relationship:

$$A_R = Q (1/\Delta T) (1/P)^{0.6}$$

wherein Q is the quantity of heat required to warm-up a  
 30 feed gas from temperature T<sub>0</sub> to T<sub>P</sub>, with T<sub>0</sub> = 100°F for all  
 examples; the ΔT is T<sub>R</sub>-T<sub>P</sub> with T<sub>R</sub> = 785°F for all examples;  
 and P is the pressure of the last reactor effluent gas and  
 is that pressure in atmospheres absolute (ata) that  
 provides for a partial pressure of steam in the effluent  
 35 gas of 2.15 ata.

Example 1 (Comparative):

-45-

This example illustrates a single pass conversion of methoxy compound, like that of the single pass process scheme employed in New Zealand. Three situations are presented: (a) wherein the methoxy component is methanol and water in a 1 to 0.35 mole ratio, (b) wherein the methoxy component is an equilibrium mixture made from the methanol-water composition above, and contains methanol, dimethyl ether and water; and (c) wherein the methoxy component is dry dimethyl ether. The recycle diluent gas for each situation comprises a mixture of C<sub>2</sub>- and C<sub>3+</sub> hydrocarbon by-product gases wherein the molar ratio of C<sub>2</sub>:C<sub>3+</sub> is 3:1. Quantities are given in lb-moles/hour which is denoted as MPH.

Feed MPH	(a) MeOH + H <sub>2</sub> O	(b) Equilibrium Mix MeOH + DME	(c) Dry DME
MeOH	28,706	7,078	—
DME	—	10,814	14,353
H <sub>2</sub> O	10037.1	20,851.1	—
C <sub>2</sub> -	342,123.3	269,194.0	253,255.5
C <sub>3+</sub>	114,041.1	89,731.3	84,451.8
Ar	10.173x10 <sup>6</sup>	9.268x10 <sup>6</sup>	5.031x10 <sup>6</sup>
Final P. (ata)	27.7385	22.342	53.4792

If instead of a recycle gas having a C<sub>2</sub>:C<sub>3+</sub> Mole ratio of 3:1 a recycle gas having a 5:1 ratio were used (which is similar to the actual New Zealand recycle gas) then the relative heat exchange surface area required for the three situations would then be: (a) 9.596 x 10<sup>6</sup>; (b) 8.735 x 10<sup>6</sup>; and (c) 4.74 x 10<sup>6</sup>. It should be noted that with respect to the use of dry DME for a single pass conversion, that the high pressure of greater than 50 ata be viewed as

-46-

undesirable in that it may promote the production of such a heavy hydrocarbon product as to cause fast cokeing, hence inactivation, of the MTG catalyst. Hence the possible attainment of greater heat exchange economies due to such high pressure operations may be illusory.

**Example 2**

An equilibrium mixture of 7,078 MPH  $\text{CH}_3\text{OH}$ , 10,814 MPH DME and 20,851 MPH  $\text{H}_2\text{O}$  is processed in accordance with the invention in a series of five MTG reactors. For the first MTG reactor of the series a portion of this methoxy content, together with an appropriate amount of  $\text{C}_2$ - and  $\text{C}_3$ + recycle gas of a  $\text{C}_2$ :- $\text{C}_3$ + ratio of 3:1 and a quantity of water to provide for a reactor outlet steam pressure of 2.15 ata is preheated to 710°F, the remainder of this methoxy content is combined with the  $\text{C}_2$ - and  $\text{C}_3$ + recycle gas of 3:1 mole ratio and preheated to the  $T_p$  temperature indicated and proportioned as fresh feed to the four subsequent MTG reactors wherein each portion is combined with the effluent gas from a preceding MTG reactor before being fed to its succeeding MTG reactor. The relative heat exchanger surface areas required for preheating the feed to the first reactor, Reactor I, and for preheating the feeds for the subsequent four reactors, Reactors II-V, are given below, as is the total of the relative heat exchange surface area required.

$T_p$ : Temperature (°F) Fresh Feed Preheat for Reactors II-V	Final Product Gas Pressure, (ata)	Relative $A_{RI}$ : Heat Exchange Surface Area, Reactor I, ( $\times 10^6$ )	Relative $A_{II-V}$ : Heat Exchange Surface Area, Reactors II-V ( $\times 10^6$ )	Total Heat Exchange Surface Area ( $\times 10^6$ )
650	11.6	0.304	3.746	4.050
600	8.6	0.902	2.098	3.000
550	7.2	1.472	1.266	2.739
500	6.1	2.006	0.828	2.834
450	5.4	2.463	0.556	3.018



-47-

400	4.8	2.893	0.382	3.276
-----	-----	-------	-------	-------

The above data demonstrates that as the fresh feed gas preheat temperature  $T_p$  is lowered, meaning that the relative proportion of the fresh feed being mixed with the hot effluent gas from a preceding reactor becomes smaller, that the contribution of the heat exchange duty requirements for preheating the first reactor feed gas to the total heat exchange duties becomes greater. As a consequence, even though of the total methoxy converted that converted in the first reactor is a small fraction, the requirements for its warm-up together with its recycle gas content is of major influence on the total heat exchange area necessary. If instead of a recycle gas having a  $C_2:C_3$  mole ratio of 3:1 a recycle gas having a mole ratio of 1:3 were used, then, using the  $T_p$  condition of 600°F for comparison, the total relative heat exchange surface area required would be  $3.760 \times 10^6$ , this being due to the lower pressure of operation required to maintain the steam partial pressure in the final effluent gas at 2.15 ata.

**Example 3:**

In a manner like that of Example 2, 14,353 MPH dry dimethyl ether is used as the alkoxy component of the feed. The following results are given:

$T_p$ : Temperature (°F) Fresh Feed Preheat for Reactors II-V	Final Product Gas Pressure (ata)	$A_R$ : Relative Heat Exchange Surface Area, Reactor I ( $\times 10^6$ )	$A_R$ II-V: Relative Heat Exchange Surface Area, Reactors II-V ( $\times 10^6$ )	$A_R$ TOTALS: Total Relative Heat Exchange Surface Area ( $\times 10^6$ )
650	28.6	0.162	1.995	2.156
600	20.6	0.489	1.139	1.628
550	16.6	0.818	0.704	1.522
500	13.6	1.137	0.469	1.606
450	12.1	1.391	0.314	1.705
400	9.6	1.869	0.149	2.018

-48-

If instead of a recycle gas having a  $C_2:C_3+$  mole ratio of 3:1 a recycle gas having a mole ratio of 1:3 were used, then, using the  $T_p$  condition of 600°F for comparison, the total relative heat exchange surface area required would be  $2.087 \times 10^6$ .

**Example 4:**

The same methoxy feed composition as in Example 2 is utilized under similar conditions except that the first MTG reactor is now operated in a mode wherein a portion of its product gas is recycled back to its inlet and mixed with feed gas thereto. Further, the feed gas to the first MTG reactor is now preheated to either 600°F or 650°F, as indicated below, and by combining it with the portion of product recycle, a combined gas stream of 710°F is formed for inlet to the first reactor.

$T_p$ :		$A_R I$ :	$A_R II-V$ :	$A_R TOTAL$ :
Reactor Feed Preheat Temp., (°F)	Final Product Gas Pressure (ata)	Relative Heat Exchange Surface Area, Reactor I	Relative Heat Exchange Surface Area, Reactors II-V	Total Relative Heat Exchange Surface Area
I @ 600°F II-V @ 600°F	8.04	$0.289 \times 10^6$	$2.022 \times 10^6$	$2.311 \times 10^6$
I @ 650°F II-V @ 600°F	8.6	$0.433 \times 10^6$	$2.010 \times 10^6$	$2.442 \times 10^6$

**Example 5:**

The same methoxy feed composition as in Example 3 is utilized under similar conditions except that the first MTG reactor is now operated in a mode wherein a portion of its product gas is recycled back to its inlet and mixed with feed gas thereto. Further, the feed gas to the first MTG reactor is now preheated to either 600°F or 650°F, as indicated below, and by combining it with the portion of product recycle, a combined gas stream of 710°F is formed for inlet to the first reactor.

-49-

5 10 15 20 25 30 35 T <sub>p</sub> :  Reactor Feed Preheat Temp., °F	Final Product Gas Pressure (ata)	A <sub>R</sub> I: Relative Heat Exchange Surface Area, Reactor I	A <sub>R</sub> II-V: Relative Heat Exchange Surface Area, Reactors II-V	A <sub>R</sub> TOTALS:  Total Relative Heat Exchange Surface Area
I @ 600°F II-V @ 600°F	18.6	1.60x10 <sup>6</sup>	1.121x10 <sup>6</sup>	1.281x10 <sup>6</sup>
I @ 650°F II-V @ 600°F	18.6	0.250x10 <sup>6</sup>	1.160x10 <sup>6</sup>	1.409x10 <sup>6</sup>

By comparison of the data presented in Example 1-5, it is apparent that the process of this invention results in a significant reduction in the heat exchange duties required for feed gas warm-up. Hence, using the equilibrium methanol-DME-H<sub>2</sub>O as the methoxy component of the feed of situation (b) of Example 1 for comparison, even at a lesser than most optimum feed gas preheat of T<sub>p</sub> = 600°F (the optimum being 550°F), as illustrated by Example 2 the same equilibrium methanol-DME-H<sub>2</sub>O component may be converted with only 32% of the heat exchange requirement of Example 1. As illustrated by Example 3, use of a dry DME as the methoxy component of the feed gas in an amount equal in methoxy equivalent to the equilibrium methanol-DME component of Example 1 allows for conversion with only 17.67% of the heat exchange requirement of Example 1. Further as illustrated in Example 3, at the feed gas preheat temperature of 600°F the operational pressure with respect to the dry DME used is 20.6 ata, hence no concern about possible coke over of the MTG catalyst should arise. Further, as illustrated in Example 5, the heat exchange requirements for processing dry DME according to the invention may be further reduced to only about 13% of that required in Example 1 by operating the first MTG reactor in a mode wherein a portion of its effluent gas is recycled back to its inlet to assist in feed gas warm-up.

-50-

Also to be realized in the practice of this invention is a reduction in the heat exchange duties required for the final step of product gas cool-down to recover its liquid hydrocarbon content. Hence, with respect to the product gas resulting in Example 1 from the conversion of the equilibrium mixture of DME-CH<sub>3</sub>OH-H<sub>2</sub>O, the final product gas after heat exchange through an adiabatic heat exchanger to warm feed gas up has a first cooldown temperature around 175°F. By contrast the final product gas resulting from the preheat T<sub>p</sub> = 600°F process of Example 2 after heat exchange through adiabatic heat exchangers to warm-up feed gas has a first cooldown temperature T<sub>x</sub> around 285°F.

With the process of this invention the final cooldown of the product gas for liquid hydrocarbon recovery requires a smaller heat exchanger because the heat exchanger needed to cool this gas operates with a larger differential temperature,  $\Delta T$ , for the needed cool down.

Although the process of this invention has been described with reference to its preferred embodiment, from this description those skilled in the art may appreciate changes and modifications that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

-51-

## CLAIMS:

1. A method of making hydrocarbon compounds by contacting an alkoxy compound with an MTG catalyst, comprising the steps of:
- combining an effluent gas product from a preceding MTG reaction zone which is at a temperature  $T_R$  with
    - (a) an alkoxy compound; and
    - (b) a diluent gas comprising a  $C_2$ - recycle gas, a  $C_3+$  recycle gas, steam, hydrogen, or mixtures thereof,
  - to form a combined gas stream wherein in the combined gas stream;
    - 1. the alkoxy compound is present in a quantity that provides an alkoxy equivalent which exceeds that added to the preceding MTG reaction zone from which the effluent product gas was formed; and
    - 2. the diluent gas composition is of a temperature and composition and is present in an amount that:
      - (a) provides for the combined gas stream to have a temperature of from about 650°F to about 720°F, and
      - (b) provides for the combined gas stream to have specific heat content that limits temperature increase of the gas stream to less than 150°F upon reaction of the alkoxy compound content thereof to hydrocarbon compounds;
      - (c) provides for a total water content following reaction of the alkoxy compound to hydrocarbon compounds that does not exceed a partial pressure of water (as steam) of 2.2 ata; and
  - contacting the combined gas stream with an MTG catalyst in a succeeding reaction zone to form a new effluent product gas.

-52-

1           2.    The method of claim 1, wherein the combined gas  
2    stream has a temperature of from about 700 to about 720°F,  
3    and the temperature increase of the gas stream is less than  
4    100°F.

1           3.    The method of claim 2, wherein the alkoxy  
2    compound is DME and the diluent gas comprises a  
3    C<sub>2</sub>- recycle gas and a C<sub>3+</sub> recycle gas in a molar ratio of C<sub>2</sub>-  
4    :C<sub>3+</sub> of from about 3:1 to about 1:3,

1           4.    The method of claim 3, wherein the diluent gas  
2    contains from about 10 to about 50 mole % of hydrogen.

1           5.    The method of claim 1, wherein from three to ten  
2    MTG reaction zones are arranged in series flow and the  
3    combined gas stream comprising the effluent gas product  
4    from a preceding MTG reaction zone and the alkoxy compound  
5    and diluent gas is at a temperature of from about 675 to  
6    about 720°F when first contacted with an MTG catalyst in a  
7    succeeding MTG reaction zone and has a specific heat  
8    content that provides for a temperature of effluent gas  
9    exiting the succeeding zone of from about 730 to about  
10   800°F.

1           6.    The method of claim 5, wherein with respect to  
2    each MTG reaction zone each combined gas stream enters each  
3    zone at substantially the same inlet temperature and each  
4    effluent gas exits each zone at substantially the same  
5    outlet temperature.

1           7.    The process of claim 6, wherein the partial  
2    pressure of water in an effluent gas does not exceed 2.2  
3    ata.

1           8.    The method of claim 1, wherein the alkoxy  
2    compound and diluent gas are preheated to a temperature of

-53-

3 from about 450 to about 550°F prior to being combined with  
4 the effluent gas product from a preceding MTG reaction  
5 zone.

1 9. The method of claim 8, wherein the combined gas  
2 stream has a temperature of from about 650 to 720°F and the  
3 temperature increase of the gas stream is about 85°F or  
4 less.

1 10. The method of claim 9, wherein the alkoxy  
2 compound is DME and the diluent gas comprises a C<sub>2</sub>- recycle  
3 gas and a C<sub>3+</sub> recycle gas in a molar ratio of C<sub>2</sub>:-C<sub>3+</sub> of from  
4 about 3:1 to about 1:3.

1 11. The method of claim 1, wherein a series of MTG  
2 reactors is employed and the combined gas stream supplied  
3 to the last MTG reactor of the series has a temperature of  
4 from about 650 to 700°F and a specific heat content that  
5 limits the new effluent product gas temperature to 760°F or  
6 less.

1 12. The method of claim 11, wherein the combined gas  
2 stream supplied to the MTG reactors other than the last MTG  
3 reactor of the series has a temperature of 710 to 730°F and  
4 a specific heat content that limits its temperature  
5 increase to a range of 70 to 90°F.

1 13. The method of claim 1, wherein a series of MTG  
2 reactors is employed and a portion of the effluent product  
3 gas from the first MTG reactor is recycled back to the  
4 first MTG reactor inlet to become admixed with feedgas to  
5 the first MTG reactor to form a combined gas stream feed to  
6 the first MTG reactor having a temperature of from about  
7 650 to 720°F and a specific heat content that limits  
8 temperature increase of the gas stream to less than 150°F.

-54-

1           14. The method of claim 13, wherein the combined gas  
2 stream feed to the first MTG reactor has a temperature of  
3 from about 650 to about 720°F and a specific heat content  
4 that limits temperature increase of the gas stream to 100°F  
5 or less.

1           15. The method of claim 1, wherein the diluent gas  
2 contains steam in an amount sufficient to provide for a  
3 partial pressure of steam in the new effluent product gas  
4 of from about 1.95 to about 2.2 ata.

1           16. The method of claim 1, wherein a series of MTG  
2 reactors is employed, and of that total quantity of alkoxy  
3 compound converted to hydrocarbon compounds, no more than  
4 20% of the total alkoxy compound is converted in the first  
5 MTG reactor of the series.

1           17. The method of claim 1, wherein each effluent gas  
2 product has a partial pressure of water of from 1.85 to 2.2  
3 ata.



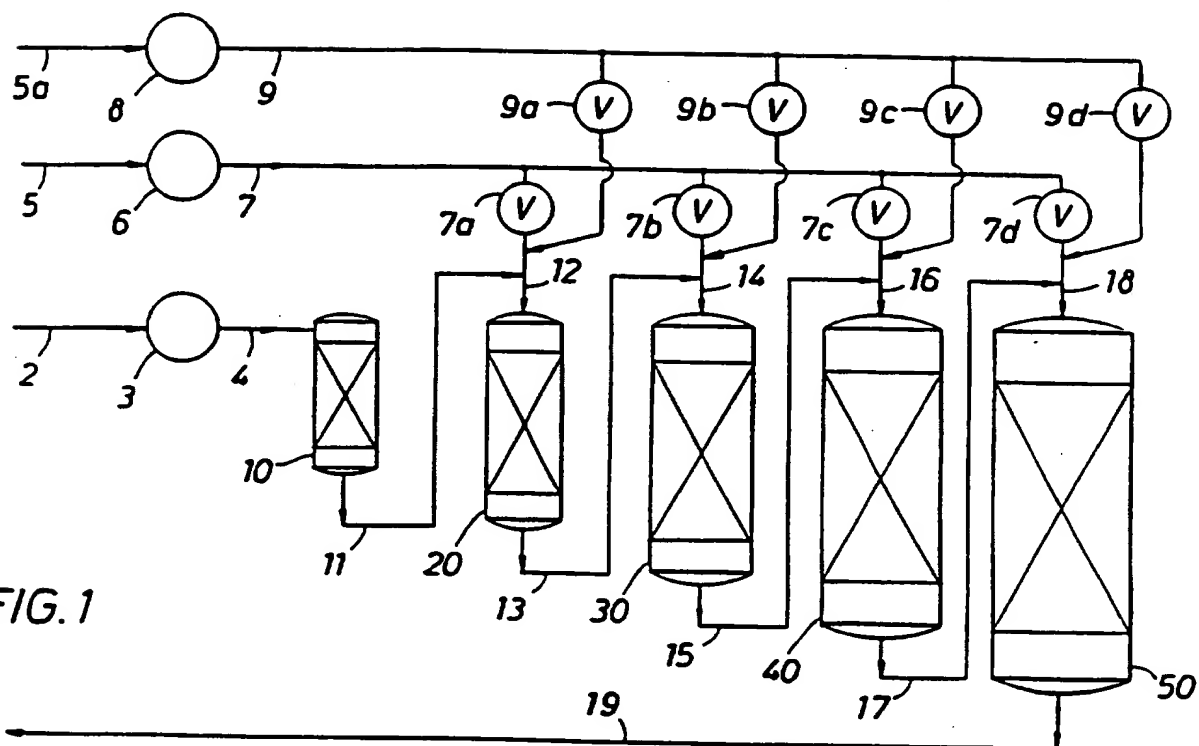


FIG. 1

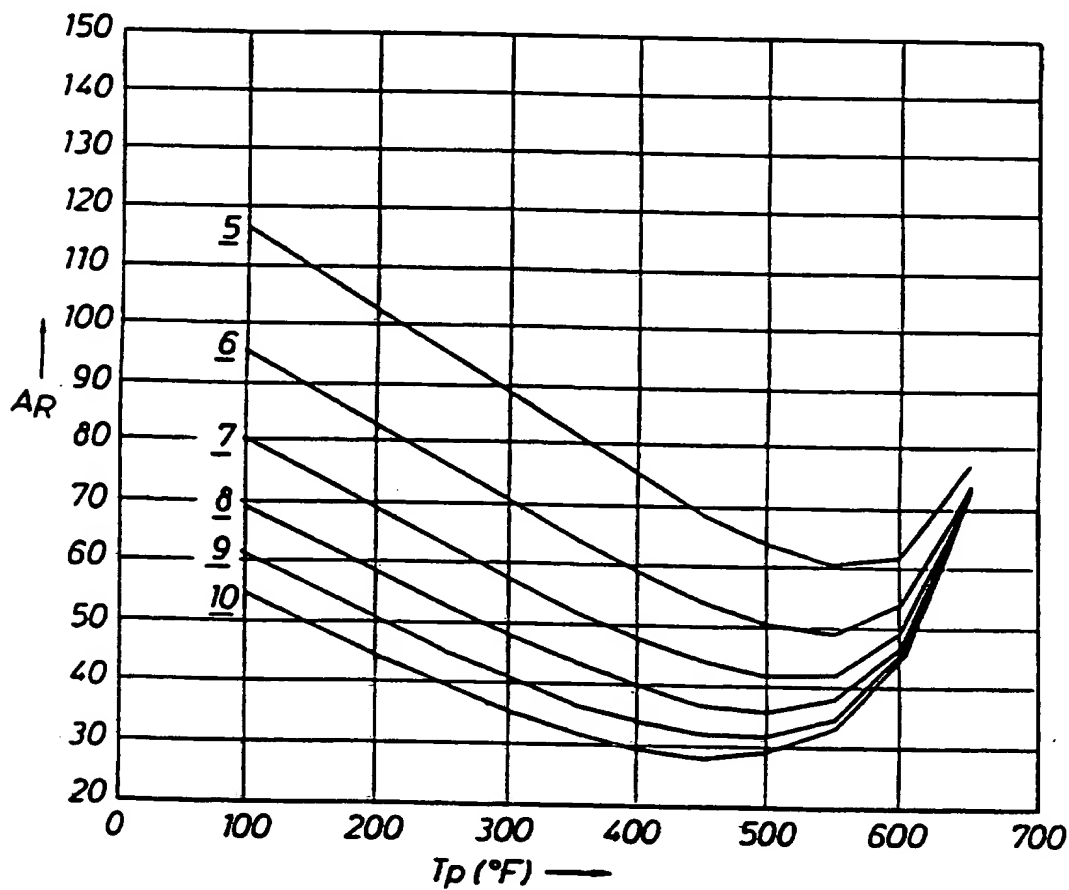


FIG. 2

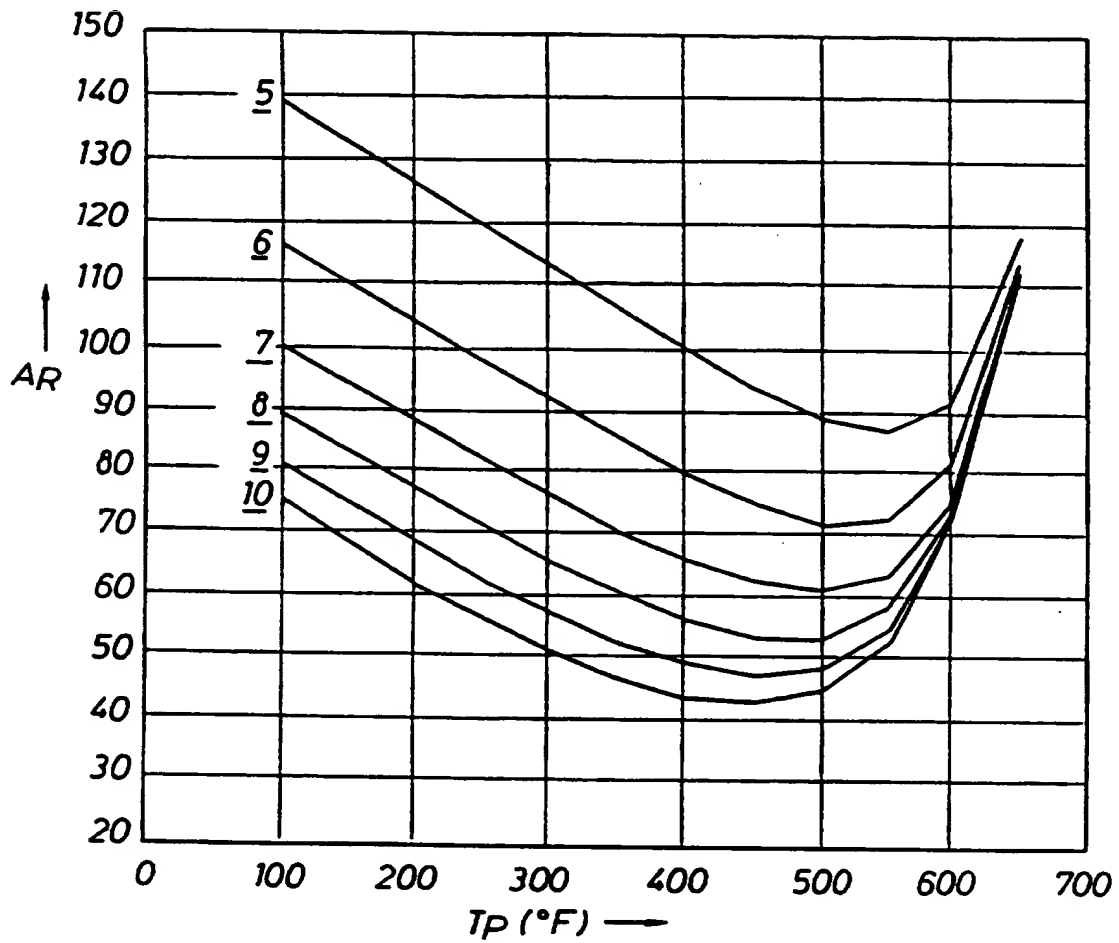


FIG. 3

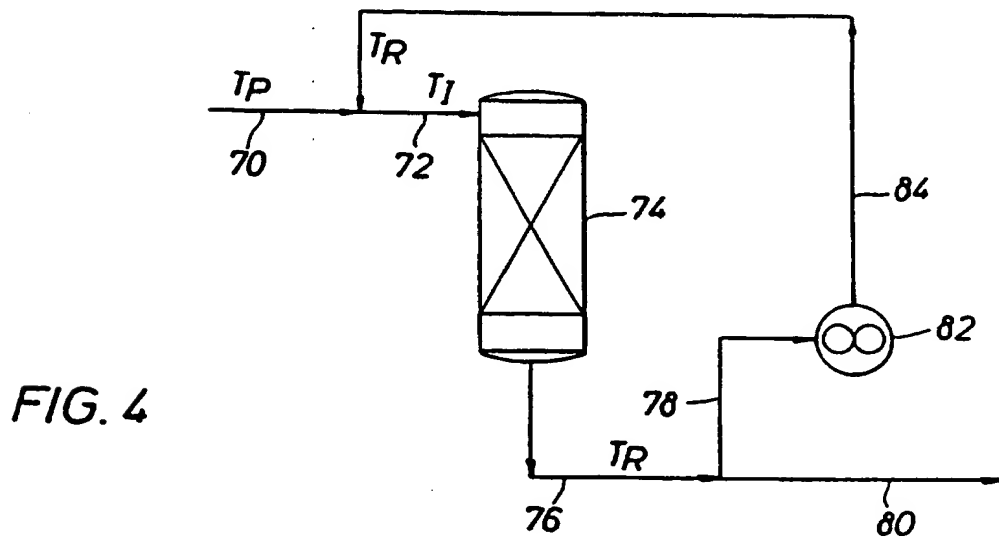


FIG. 4

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/14397

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C07C 1/20,1/22

US CL : 585/408,469,639

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/408,469,639,315,733

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,035,430 (DWYER ET AL) 12 July 1977, col. 8 lines 66-69; col. 9, lines 1-9; col. 9 lines 13-20	1-4,11-17
Y	US,A, 4,404,414 (PENICK ET AL) 13 September 1983, col 6., lines 36-58; col. 9, lines 39-53, especially, line 47.	1-4,11-17
A	US, A, 4,547,602 (TABAK) 15 October 1985	
A	US, A, 3,931,349 (KUO) 06 JANUARY 1976	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, each combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 FEBRUARY 1996

Date of mailing of the international search report

20 MAR 1996

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

GLENN CALDAROLA

Telephone No. (703) 305-6118

Form PCT/ISA/210 (second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/14397

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS ,

search terms: (serial,plural,sequen?,casade?);(reactor?,cataly?,stage?);(585\*408,469,639,733,315/ccls)

1 / 2

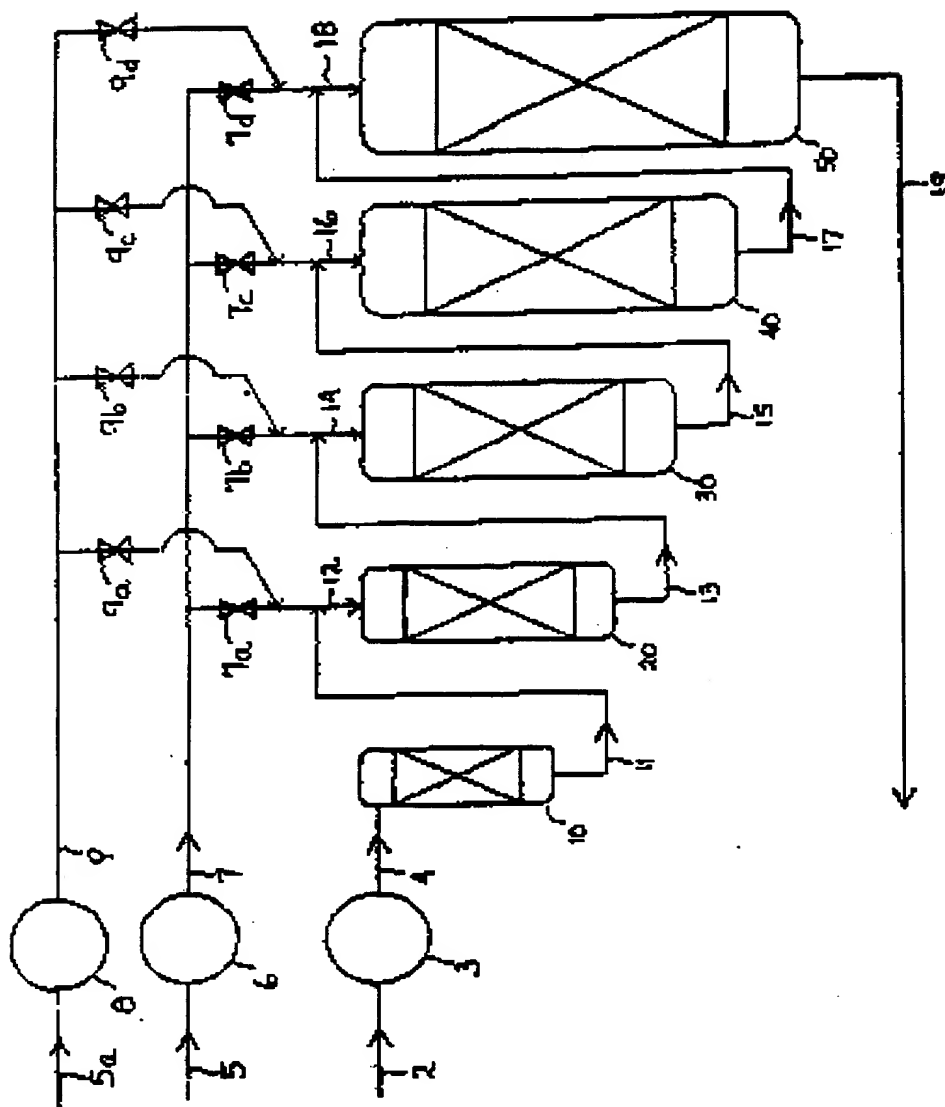


Fig 1

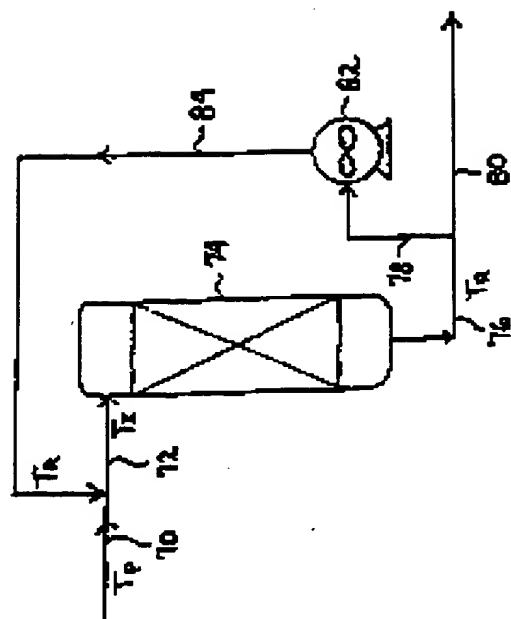


Fig 4

2 / 2

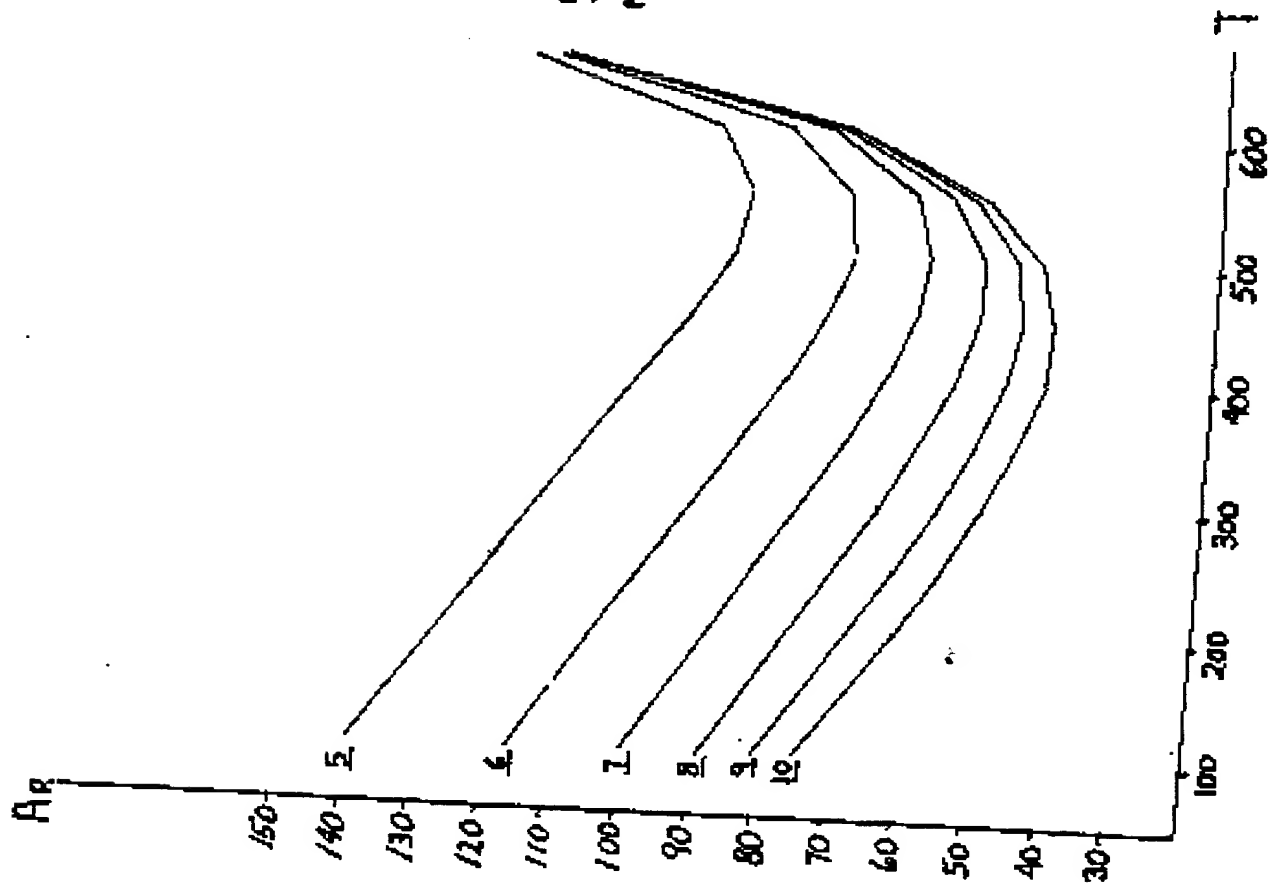


Fig. 2

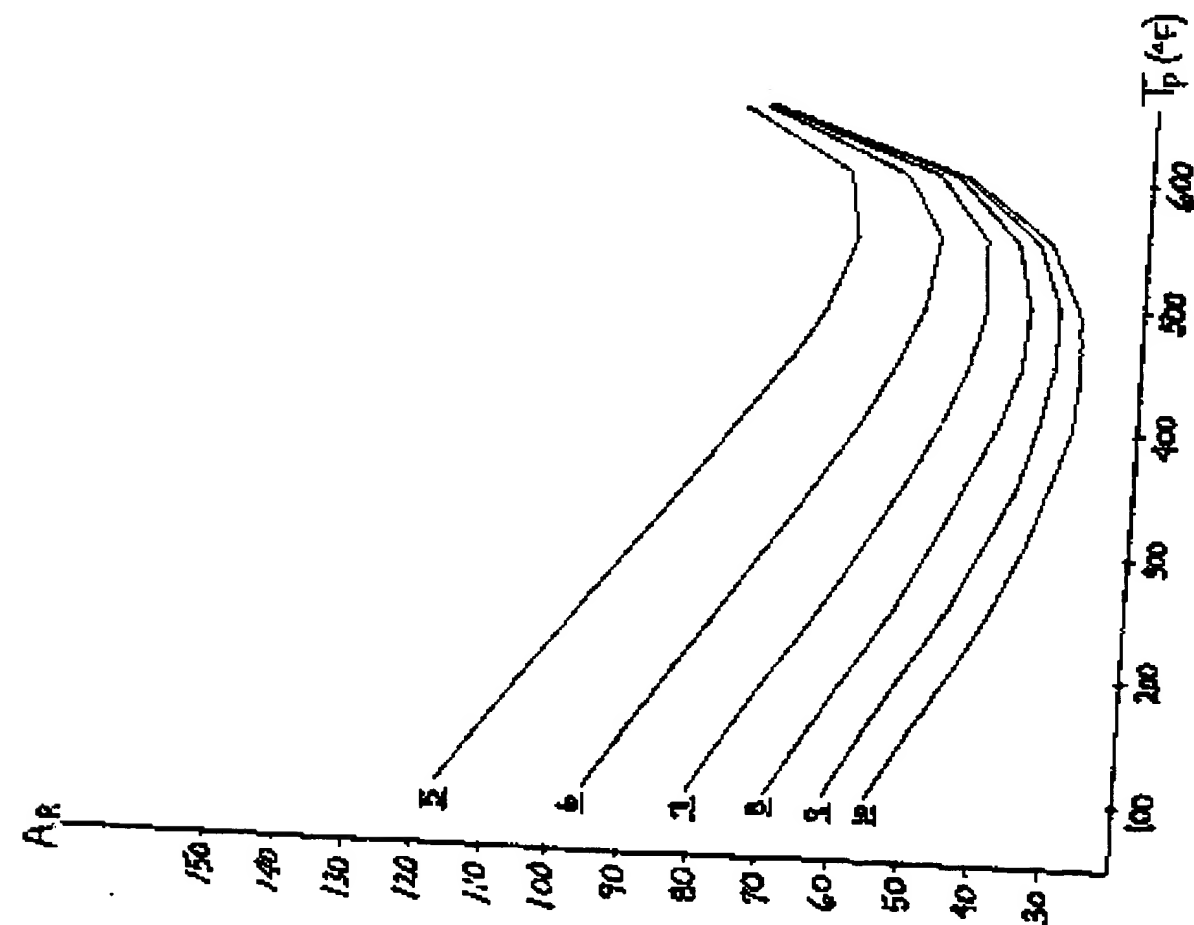


Fig. 3

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**